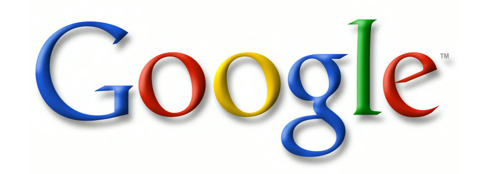
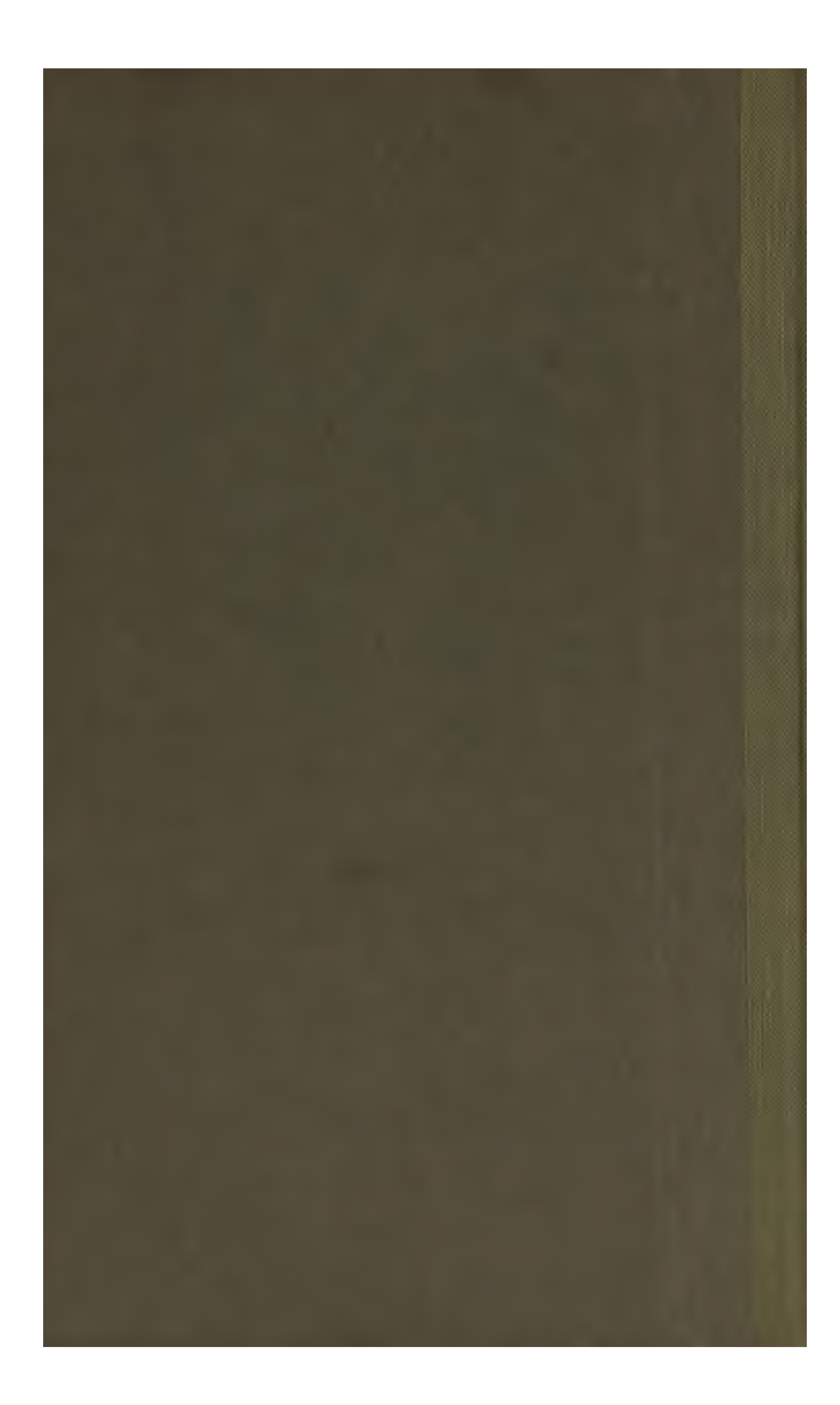
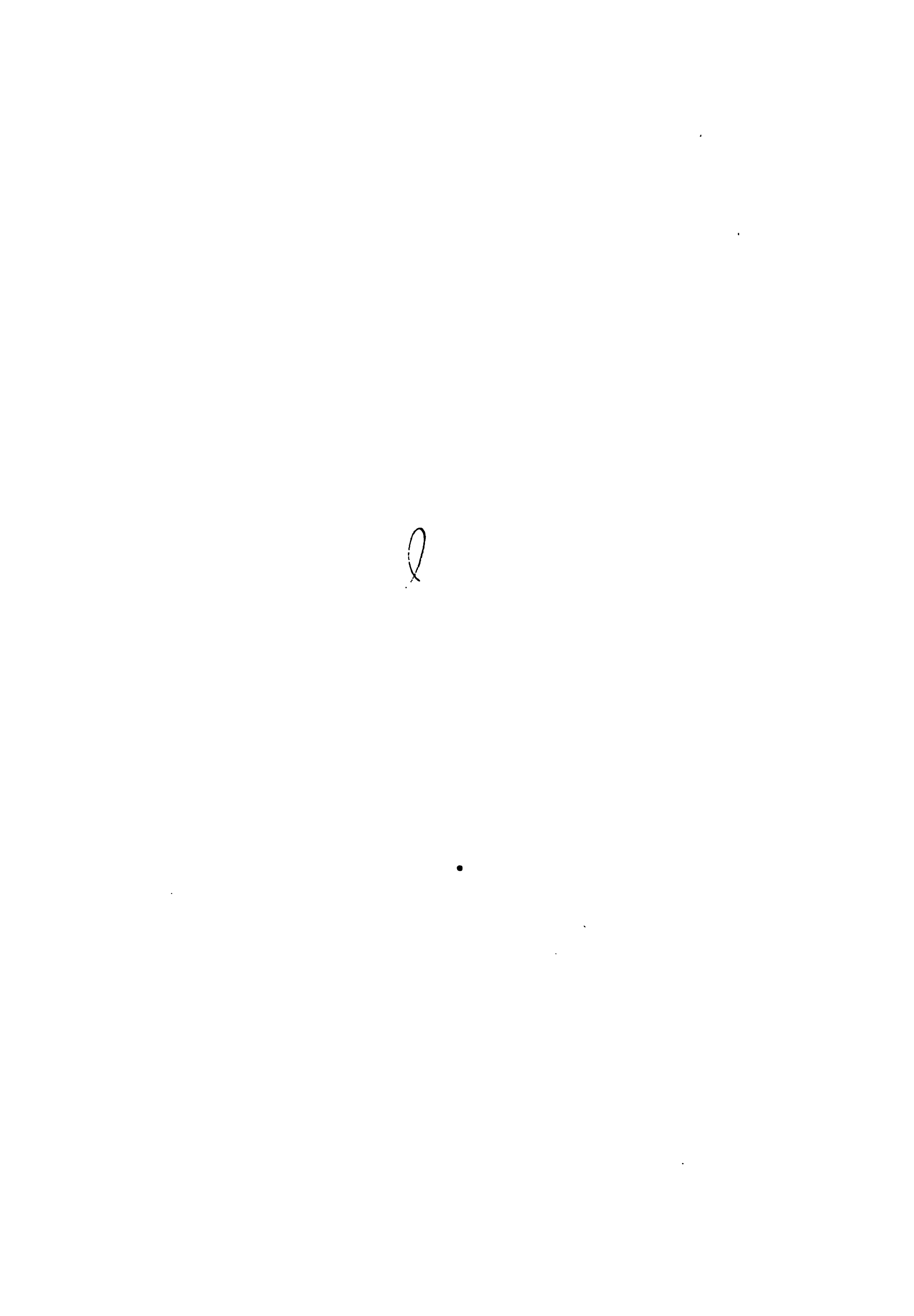

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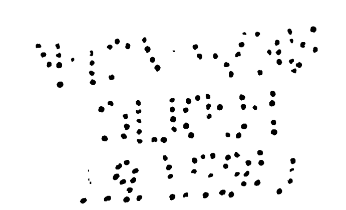
A SYSTEMATIC QUALITATIVE CHEMICAL ANALYSIS

A Theoretical and Practical Study of Analytical Reactions of the More Common Ions of Inorganic Substances

BY

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PREFACE

THE author believes that a course in Qualitative Analysis should not only train the student in accurate and careful manipulation and so prepare him for the more careful work necessary in Quantitative Analysis, but should also serve to extend and supplement his knowledge of General and Theoretical Chemistry. To this end an attempt has been made to present the theoretical and practical parts in such a way that the student will understand the significance and see the practical applications of the theoretical part.

The book has been divided into four parts, including the Appendix. Part I consists of the Introduction and Laboratory Suggestions. In the Introduction is given a brief discussion of the Ionic Theory and Law of Mass Action, as applied to the principles involved in Qualitative Analysis, and reference to its various sections is made throughout the text. Part II consists of Preliminary Experiments, Method of Analysis, Discussion and Review Questions on the metal ions. In order that the student may get a comparative idea of the actions of the different metal ions in a group toward a given reagent, the Preliminary Experiments are arranged in a manner which differs somewhat from the usual one and in order that he may not be confused by too many reactions, only those reagents used in the Method of Analysis are employed. Preliminary Experiments whose reactions may not be clear are followed by Notes. In the Method of Analysis an attempt has been made to give clear and concise directions for procedure only, all explanations and conditional pro-

cedures being placed together under Discussion, following each group or sub-group. It is believed that by frequent reference to this the student's attention will be brought more effectively to the theoretical explanations and to the reasons for careful work. In so far as practicable, only Quantitative reactions have been given and only those methods have been used which have been thoroughly tested. Part III consists of Method of Analysis, Discussion and Review Questions on the acids.

A new method of anion analysis is given which follows in general the method of procedure in metal analysis, in that a single sample is taken for analysis, and largely by means of precipitation methods, the separation and detection of anions are made. Many of the same reactions used in the course of metal analysis are also employed. For these reasons no preliminary experiments are given, the author having found that students are able to understand and follow the directions in the analysis of "unknowns." In the Appendix are given directions for the preparation of reagents and test solutions, also tables of solubilities and atomic weights of the more common elements.

In the preparation of this text the author has made use of information from all convenient sources, including such textbooks on Qualitative Analysis as those of Treadwell-Hall, A. A. Noyes, Julius Stieglitz, and W. A. Noyes, to whom he wishes to acknowledge his indebtedness. Acknowledgment is also due to Dr. J. F. G. Hicks, Stanford University, and to Miss M. Dewar, University of Nevada, for helpful criticism and assistance.

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A SYSTEMATIC QUALITATIVE CHEMICAL ANALYSIS

PART I

INTRODUCTION

1. In his study of General Chemistry the student has become somewhat familiar with the more important elements, their preparation, physical properties and some of their principal compounds. In his laboratory work he has become acquainted with the different types of chemical reactions; viz., combination, decomposition, displacement, double decomposition, oxidation-reduction, etc. He has learned that certain reactions are reversible, that others are non-reversible, and that the point of equilibrium in reversible reactions is influenced by the relative amounts of the substances entering into the reaction.

2. "**Qualitative Analysis** treats of the identification of matter," while *Quantitative Analysis*, as its name implies, deals with its quantitative determination. An efficient system of qualitative analysis should consist not only in finding out what substances are present and what are absent but also in obtaining an estimate of the relative quantity of each constituent present. In order to accomplish this with accuracy and certainty the analyst should know the principle involved in the chemical actions concerned, the reason for each reagent used, the result it produces and how this result is brought about. For the purpose of Qualitative Analysis it is usually desirable

and often necessary to separate the substances from each other and then apply some characteristic chemical reaction which can be easily and accurately recognized.

3. In the course of this outline the following terms will be used frequently, and the student should become familiar with them and their meaning at the outset.

(*a*) **A Reagent** is a substance which produces a known reaction and is used for the purpose of obtaining a desired result.

(*b*) **A solution** is a homogeneous mixture, the properties of which change gradually with change in composition. Aqueous solutions are of most importance and are used almost exclusively in this outline. The student should learn, early in his course, to distinguish between solutions and colloidal suspensions.

(*c*) **Precipitate** is a term usually applied to a solid substance which separates from solution on the addition of a reagent. It may be finely divided so that it settles very slowly and is not held by a filter paper. Such a precipitate is termed "colloidal." Precipitates are distinguished as crystalline, flocculent, curdy, colloidal, etc.

(*d*) **Residue** is a term usually applied to that portion of a solid left undissolved by a given reagent or solvent.

(*e*) **Filtration** consists in the mechanical separation of a solid from a liquid, by means of a suitable screen, which allows only the liquid to pass through. The liquid passing through is known as the **filtrate**, while the solid remaining on the filter is called the **precipitate** or **residue.**

(*f*) **Decantation** consists in carefully pouring-off the liquid from the solid which has been allowed to settle. This operation is employed with crystalline precipitates where a thorough washing is

essential. The washing liquid, usually pure water in small portions, is thoroughly mixed with the solid and set aside until the undissolved portion has settled. The clear supernatant liquid is then poured off. The operation is repeated until the solid is sufficiently washed. In most of the operations of Qualitative Analysis sufficient washing may be obtained by blowing a fine stream of water from a wash bottle on to the filter containing the precipitate or residue.

(*g*) **Digestion** is the term applied to a reaction between two or more substances that are mixed, hot or cold, and allowed to stand for some time with occasional stirring.

4. Ionic Theory.—In his study of the effect of the solute on the properties of solutions, Raoult showed that if a non-volatile substance is dissolved in pure water certain properties, viz., boiling-point, freezing-point, osmotic pressure and vapor pressure, vary with the concentration of the solute. Furthermore, he showed that equimolecular proportions of certain substances produce an equal effect on these properties, e.g., one molecular weight of cane sugar ($C_{12}H_{22}O_{11} = 342$ gms.) or of glucose ($C_6H_{12}O_6 = 171$ gms.) or of glycerine ($C_3H_5(OH)_3 = 92$ gms.), when dissolved in 10 liters of water, lowers the freezing-point 0.186° C. and raises the boiling-point 0.052° C. From Avogadro's Law we learn that equal volumes of gases under the same conditions of temperature and pressure contain an equal number of molecules. A careful study of solutions has shown that a dissolved substance possesses properties similar to those of a gas having the same molecular concentration. A consideration of these and other facts leads to the conclusion that equimolecular proportions of all substances, whether liquid, solid or gas, contain equal numbers of molecules. The change in freezing-point, boiling-point, etc., is therefore

proportional to the number of molecules or particles of solute dissolved in a given amount of the solvent. Examination of a great variety of substances in different solvents has demonstrated the truth of this conclusion.

5. When an acid, base or salt is dissolved in pure water, the change in freezing-point, boiling-point, etc., is greater than would be expected from the general rule. In their chemical relations these compounds show a marked difference from those which follow the rule. Their reactions in solution are very rapid. In double decomposition reactions they seem to be composed of two or more radicals which act largely independently of each other. They are the only substances whose solutions conduct electricity. Furthermore, there are certain colored salts, e.g., copper chloride ($CuCl_2$, greenish-yellow), copper bromide ($CuBr_2$, reddish-brown), and copper sulphate ($CuSO_4$, blue), whose solutions on being diluted finally assume the same color (blue). In explanation of these facts Arrhenius, in 1885, proposed what is known as the "*Ionic Theory*." It assumes that acids, bases and salts, when dissolved in water, dissociate into two or more radicals or particles, that these particles carry an electric charge and that an equilibrium exists between the undissociated particles and their dissociation products.

6. When an electric current is passed through a solution of an acid, e.g., HCl, H_2SO_4, etc., the hydrogen collects around the negative electrode and the remaining radical, (Cl), (SO_4), etc., collects around the positive electrode. When the current is made to pass through a solution of a base, e.g., NaOH, KOH, etc., the hydroxide radical (OH) proceeds toward the positive electrode while the metal radical is carried toward the negative electrode. In the case of salt solutions, e.g., NaCl, Na_2SO_4, etc., the metal and acid radicals act in the same manner toward the electric current as if they were present as the base and acid respectively. A radical, therefore, proceeding under the influence of an electric current, always moves toward

the same pole regardless of whether it is present as an acid, base or salt. From this it follows that the hydrogen radical must carry a positive electric charge and the hydroxide radical a negative charge. Similarly the metal radical will be charged positively and the acid radical negatively. A radical bearing an electric charge is called an *ion* and the process by which ions are formed from the undissociated molecules is called *ionization.*

7. Kinetic Theory and Ionic Equilibrium.—When an acid, base or salt goes into solution the influence of the water causes it to dissociate, with the formation of positively and negatively charged ions. On the basis of the kinetic theory we may assume that the continual movement and jostling about of the molecules causes them to split apart or dissociate. At the same time the dissociated particles or ions will collide with each other with the result that some of them will again unite to form undissociated molecules. At first the former reaction, dissociation, is more rapid, but as the number of ions increases their union becomes more frequent until after a time the rate of the two reactions will be equal, i.e., the number of molecules dissociating in a unit of time will be just equal to the number formed by the union of ions. When this condition is established the reaction is said to be in equilibrium. It is expressed by means of an equation as follows:

$$AB \rightleftharpoons A + B$$

8. Degree of Ionization.—Experiment has shown that the proportion of a substance existing in the form of ions depends on its concentration in the solution, the more dilute solution having the higher per cent of ionization. This is explained on the basis of the kinetic theory, as follows: In concentrated solutions the ions are comparatively close together and collisions will be relatively frequent, while in the more dilute solutions the ions are necessarily farther apart and the time between collisions will be greater. The result is that fewer of them will

unite, per unit of time, to form non-ionized molecules. The per cent existing in the form of ions must therefore increase with increased dilution, a condition which agrees with experimental data. While it has been found that the degree of ionization in solutions made from salts is relatively high and approximately the same[1] for all salts of the same concentration, a wide variation exists in the cases of acids and bases.

9. The degree of ionization in normal and 0.1 normal solutions of the more common acids, bases and salts is given in the following table:

Acids	Per Cent Ionized		Bases	Per Cent Ionized	
	N soln.	0.1 N oln.		N soln.	0.1 N soln.
H^+Cl^-	78.4	90	K^+OH^-	77	86
$H^+NO_3^-$	82	90	Na^+OH^-	73	86
$H^+HSO_4^-$	51	60	$Ba^{++}(OH)_2^-$	69	......
$H^+HC_2O_4^-$	....	50(0.2 N) (soln.)	$NH_4^+OH^-$	0.4	1.31
$H^+C_2H_3O_2^-$	0.41	1.3			
$H^+HCO_3^-$	0.17				

Salts

Approximate degree of ionization for salts in 0.1 N solution

Type M^+A^-(e.g., KCl)................ 86 per cent
Type $M^{++}A_2^-$(e.g., $BaCl_2$)............. 72 per cent
Type $M_2^+A^{--}$(e.g., K_2SO_4)............. 72 per cent
Type $M^{++}A^{--}$(e.g., $BaSO_4$)............ 45 per cent

10. Law of Mass Action.—From a careful study of chemical equilibria and rate of chemical action Gulberg and Waage showed that the speed of a reaction is directly proportional to the concentration of the reacting substances. This is known as the *Law of Mass Action.*

[1] Notable exceptions to this rule are $HgCl_2$ and $Pb(C_2H_3O_2)_2$, whose per cents of ionization are relatively very small.

When sodium chloride (NaCl) is dissolved in water the following equilibrium is established;

$$NaCl \rightleftharpoons Na^{+} + Cl^{-}$$

Since the number of NaCl molecules which dissociate in a unit of time is proportional to the concentration of the undissociated molecules, the speed of dissociation may therefore be stated mathematically as follows:

$$S_1 = f_1 C_{NaCl}$$

where S_1 = speed of dissociation, C_{NaCl} = molar concentration of undissociated NaCl and f_1 = the proportionality constant. In like manner the number of Na^{+} and Cl^{-} which unite to form the undissociated NaCl per unit of time is proportional to the product of their concentrations and may be expressed mathematically as follows:

$$S_2 = f_2 C_{Na^{+}} \cdot C_{Cl^{-}}$$

where S_2 = speed of union, $C_{Na^{+}}$ and $C_{Cl^{-}}$ = the concentrations of the Na^{+} and Cl^{-} respectively and f_2 = the proportionality constant. When equilibrium is established the speeds of the opposing actions must be equal; therefore

$$f_1 C_{NaCl} = f_2 C_{Na^{+}} \cdot C_{Cl^{-}}$$

and by transposition

$$\frac{C_{Na^{+}} \cdot C_{Cl^{-}}}{C_{NaCl}} = \frac{f_1}{f_2}$$

Since f_1 and f_2 are constants their ratio must be constant and

$$\frac{C_{Na^{+}} \cdot C_{Cl^{-}}}{C_{NaCl}} = K$$

where K is a constant. This is the mathematical statement of the Law of Mass Action as applied to the ionization of sodium chloride, and shows that the product of the concentrations of the ions in the solution divided by the concentration of the non-ionized molecules is a constant

quantity which is independent of the source of the ions. K is known as the ionization constant. For highly ionized substances that are very soluble K varies considerably with the change in concentration, but for slightly ionized substances and those that are difficultly soluble it remains practically the same. The following examples will serve to illustrate.

Experiment has shown that in a molar solution of acetic acid ($HC_2H_3O_2$), 0.41 per cent of the acid is in the form of ions while 99.59 per cent of it remains in the non-ionized state. The ion concentration, therefore, is $1 \times 0.0041 = 0.0041$ and that of the non-ionized portion is $1 \times 0.9959 = 0.9959$, i.e., the condition of equilibrium in a liter of 1 molar acetic acid becomes

$$\begin{matrix} HC_2H_3O_2 & \rightleftharpoons & H^+ & + & C_2H_3O_2^- \\ (0.9959 \text{ mol}) & & (0.0041 \text{ mol}) & & (0.0041 \text{ mol}) \end{matrix}$$

Substituting these values in the Mass Law equation

$$\frac{C_{H^+} \cdot C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K$$

K is found to have the value

$$\frac{0.0041 \times 0.0041}{0.9959} = 0.0000169$$

If the above molar solution is diluted to ten times its original volume the proportion of acid that exists in the form of ions will increase to 1.3 per cent. Using this value we obtain $0.1 \times 0.013 = 0.0013$ for the ion concentration and $0.1 \times 0.987 = 0.0987$ for the concentration of the non-ionized portion. Substituting these values in the Mass Law equation

$$\frac{C_{H^+} \cdot C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = \frac{0.0013 \times 0.0013}{0.0987} = 0.0000171$$

a value is obtained which is in very good agreement with that obtained in the molar solution.

In the case of ammonium hydroxide (NH_4OH) experi-

ment shows that a 0.1 molar solution is 1.31 per cent ionized. The ion concentration, therefore, is $0.1 \times 0.0131 = 0.00131$ and the concentration of the non-ionized molecules is $0.1 \times 0.9869 = 0.09869$. Substituting these values in the mass-law equation we obtain for the ionization constant

$$\frac{C_{NH_4^+} \cdot C_{OH^-}}{C_{NH_4OH}} = \frac{0.00131 \times 0.00131}{0.09869} = 0.0000173$$

In a 0.01 molar solution the per cent of ionization has been found to be 4.07, from which we obtain the following equation

$$\frac{(0.01 \times 0.0407) \times (0.01 \times 0.0407)}{(0.01 \times 0.9593)} = K = 0.0000172$$

11. Solubility Product.—Since precipitation methods play an important part in Analytical Chemistry, a consideration of the mass law in its relation to saturated solutions is of considerable importance. When a substance, such as sugar or salt, is placed in contact with a liquid, some of the molecules of the solid enter the liquid and in accordance with the kinetic theory move about in all directions within the liquid. After a time some of them will return to the solid, and as more of the solid dissolves the number of molecules returning to the solid will increase, until the number entering the liquid and the number leaving it in a unit of time are equal. When this condition prevails **equilibrium** is established and the number of dissolved molecules (molar concentration) is a constant. The solution is said to be saturated. It follows, therefore, that in a saturated solution of an acid, base or salt there must be an equilibrium between the undissolved solute, the undissociated molecules in solution and its ions. In the case of the difficultly soluble salt, AgCl, this equilibrium may be expressed as follows:

$$\underline{AgCl}\,^{1} \rightleftharpoons AgCl \rightleftharpoons Ag^+ + Cl^-$$

[1] A line (________) drawn beneath a symbol will be used to denote the undissolved solid, precipitate or residue.

and the equilibrium for the Law of Mass Action becomes

$$\frac{C_{Ag^+} \cdot C_{Cl^-}}{C_{AgCl}} = K$$

Since the solution is saturated, C_{AgCl} is a constant quantity and

$$C_{Ag^+} \cdot C_{Cl^-} = K \cdot C_{AgCl} = \mathbf{K}$$

Therefore, in a saturated solution of a given ionogen the product of the concentration of its ions [1] is a constant and is called the **Solubility Product.**

In the following table are placed the solubility products at 18° C. of some of the more common substances met with in qualitative analysis.

Substance	**K**	Substance	**K**
HgS	$4.0 \cdot 10^{-53}$	Ag_2CrO_4	$1.0 \cdot 10^{-12}$
CuS	$8.5 \cdot 10^{-45}$	$Mg(OH)_2$	$3.4 \cdot 10^{-11}$
CdS	$3.6 \cdot 10^{-29}$	$BaCrO_4$	$1.6 \cdot 10^{-10}$
PbS	$4.2 \cdot 10^{-28}$	$BaSO_4$	$9.0 \cdot 10^{-10}$
CoS	$3.0 \cdot 10^{-26}$	AgCl	$8.7 \cdot 10^{-9}$
NiS	$1.4 \cdot 10^{-24}$	CaC_2O_4	$1.7 \cdot 10^{-9}$
ZnS	$1.2 \cdot 10^{-23}$	$CaCO_3$	$2.8 \cdot 10^{-9}$
FeS	$1.5 \cdot 10^{-19}$	$BaCO_3$	$1.9 \cdot 10^{-9}$
MnS	$1.4 \cdot 10^{-15}$	$PbSO_4$	$1.0 \cdot 10^{-8}$
$MgNH_4PO_4$	$2.5 \cdot 10^{-13}$	$SrSO_4$	$2.8 \cdot 10^{-7}$

The ion product, and therefore the solubility, of a substance may be altered in the following ways:

(*a*) By the addition of a reagent containing a common ion.

(*b*) By addition of a reagent which forms with one of the ions a slightly ionized compound.

[1] This is true in the case of ionogens consisting of one cation and one anion. In other cases the solubility product should contain the ion concentration raised to a power equal to the number of ions that are alike in its formula, e.g., the solubility product for $PbCl_2$ should be written $C_{Pb^{++}} \cdot C^2_{Cl^-} = \mathbf{K}$.

(c) By addition of a reagent which unites with one of the ions to form a complex ion.
(d) By addition of a reagent which alters the charge on one on the ions. (Oxidation and reduction.)
(e) By addition of a strong acid or strong base to an amphoteric substance.

12. Common Ion.—When a soluble chloride, such as HCl or NH_4Cl, is added to an acid solution of a silver salt, silver chloride (AgCl) is precipitated. The solution will be saturated with respect to silver chloride when the ion product, $C_{Ag^+} \cdot C_{Cl^-}$, reaches the solubility product value, $\mathbf{K}_{AgCl}$, for silver chloride. Any further addition of chloride tends to increase the ion product above the solubility product value. This in turn disturbs the equilibrium

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

so as to decrease the concentration of silver ions. Since the concentration of the silver ion can be decreased only by uniting with chloride ions to form non-ionized AgCl the solution tends to become supersaturated with respect to AgCl molecules. Some of the silver chloride will therefore be precipitated and the following equilibrium will result:

$$\underline{AgCl} \rightleftharpoons AgCl \rightleftharpoons Ag^+ + Cl^-$$

At 25° the ion concentration of a saturated solution of silver chloride has been found to be $1.2 \cdot 10^{-5}$. From this is obtained for the solubility product,

$$C_{Ag^+} \cdot C_{Cl^-} = K = 1.44 \cdot 10^{-10}$$

If to 1 liter of this solution 0.01 mole (0.535 gm.) of ammonium chloride (NH_4Cl) (86 per cent ionized) is added, the concentration of the chloride ions is increased by $0.01 \times 0.86 = 0.0086$, and C_{Cl^-} will be $0.0086 + 0.000012 = 0.008612$ or about 700 times as large as in the original solution. Since $C_{Ag^+} \cdot C_{Cl^-} = 1.44 \cdot 10^{-10}$ it will be seen

that the concentration of silver ions must decrease to about $\frac{1}{700}$ of its original value. The student should especially note that the completeness with which a given ion may be removed from solution in this way depends on the concentration of the non-ionized molecules in a saturated solution, since their concentration is not decreased by addition of a common ion. Complete precipitation, from the standpoint of Analytical Chemistry, is obtained only when this value is very small.

13. Slightly Ionized Compounds.—The preceding paragraph has shown how the addition of a common ion may be used to remove a given ion from solution when the compound formed is difficultly soluble. In the same way a given ion may be reduced to almost nothing when the compound formed is soluble but very slightly ionized. If to a 0.1 molar solution of acetic acid ($HC_2H_3O_2$) (1.3 per cent ionized) a 0.1 mole of some soluble acetate, such as sodium acetate ($NaC_2H_3O_2$) (86 per cent ionized), is added, the large excess of acetate ions tends to increase the speed of union of H^+ and $C_2H_3O_2^-$ and so shifts the equilibrium $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$ to the left. From the equation

$$\frac{C_{H^+} \cdot C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = \frac{0.0013 \times 0.0013}{0.0987} = 1.7 \cdot 10^{-5}$$

it will be seen that $C_{HC_2H_3O_2}$ cannot be appreciably increased owing to the small concentration of H^+ available. The product $C_{H^+} \cdot C_{C_2H_3O_2^-}$ must therefore recover approximately its original value. Since on the addition of sodium acetate, $C_{C_2H_3O_2^-}$ becomes $0.086 + 0.0013 = 0.0873$ or about 60 times its original value, C_{H^+} must be decreased to about $\frac{1}{60}$ of its former magnitude. While the per cent of ionization of the salt must also decrease because of the presence of the acetate ions from the acid, the amount is negligible in proportion to its original value since the number of acetate ions is relatively so few (0.0013 : 0.086). Therefore when the compound formed is soluble a given

ion can be reduced to almost nothing only when the compound is very slightly ionized.

14. **Hydrolysis.**—Pure water ionizes to a slight extent into H^+ and OH^-. Although the ions of water may be neglected when all the substances concerned in a given reaction are highly ionized, they become quite appreciable and must be taken into consideration when the reaction involves substances that are very slightly ionized or difficultly soluble. Experiment has shown that the concentration of H^+ and therefore of OH^+ in pure water at 25° is 10^{-7}. The concentration of the non-ionized molecules is therefore very large in comparison and may be considered constant. From the Law of Mass Action, then, the product of the concentrations of the ions becomes a constant. Since $C_{H}^+ = C_{OH}^- = 10^{-7}$ we have for the ion product $C_{H}^+ \cdot C_{OH}^- = 10^{-14}$. In any solution, therefore, the concentration of H^+ multiplied by the concentration of OH^- must equal the ion product constant, 10^{-14}. An increase of H^+ must result in a decrease of OH^- and vice versa.

When sodium acetate ($NaC_2H_3O_2$), a highly ionized salt, is dissolved in water the concentration of $C_2H_3O_2^-$ may become so large that its product with the H^+ of the water will exceed the ionization value for the slightly ionized acetic acid ($HC_2H_3O_2$). Some of the $C_2H_3O_2^-$ and H^+ therefore unite to form the non-ionized acid which momentarily reduces the ion product for water below 10^{-14}. The result is that more water ionizes until the product $C_{H}^+ \cdot C_{OH}^-$ again reaches 10^{-14}. The student should note that C_{H}^+ is now less than C_{OH}^- and therefore the solution becomes basic. On the other hand, if ferric chloride ($FeCl_3$) is dissolved in water the concentration of Fe^{+++} from the highly ionized salt, multiplied by the concentration of OH^- already present in the water, may exceed the ionization value for the very slightly ionized ferric hydroxide and form non-ionized $Fe(OH)_3$. The ion product for water is thus momentarily reduced below

10^{-14}. More water must therefore ionize until the product $C_{H^+} \cdot C_{OH^-} = 10^{-14}$ is reached. C_{H^+} is now greater than C_{OH^-} and the solution reacts acid. It will be seen therefore that the ions of water must be taken into consideration when a substance is involved either one of whose ions may unite with one of the ions of water to form a very slightly ionized compound. Should the compound be difficultly soluble the equilibrium may be shifted to completion and a given ion removed from solution.

15. Complex Ion.—When ammonium hydroxide is added to a solution of a copper salt, copper hydroxide ($Cu(OH)_2$) is at first precipitated, but on the addition of an excess of the reagent the $Cu(OH)_2$ precipitate is dissolved and a deep blue solution is obtained. It would seem from the foregiong discussion and the principle of the Law of Mass Action that an excess of the reagent should produce a more complete precipitation as was found to be the case with silver chloride (see **12** above). It will be remembered from the study of general Chemistry that when ammonia (NH_3) is dissolved in water only a small portion of it reacts with the water to form ammonium hydroxide (NH_4OH), the greater part of it remaining in the solution as ammonia (NH_3). The following equilibrium must therefore exist in the solution:

$$H_2O + NH_3 \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-.$$

An examination of the deep-blue copper solution shows the presence of the complex ion $Cu(NH_3)_4^{++}$. From the principle of the solubility product

$$C_{Cu^{++}} \cdot C^2_{OH^-} = \mathbf{K},$$

it is evident that any increase of OH^- above that necessary to reach the solubility product for $Cu(OH)_2$ must result in a decrease in the Cu^{++} concentration. The concentration of the Cu^{++} may be decreased either by the formation of non-ionized $Cu(OH)_2$ and consequent precipitation or by its union with free ammonia to form the complex

ion $Cu(NH_3)_4^{++}$. The high proportion of free ammonia and the slight dissociation of the complex ion $Cu(NH_3)_4^{++}$, both influence the equilibrium toward the formation of the complex ion, hence the net result is that the equilibrium

$$\underline{Cu(OH)_2} \rightleftharpoons Cu(OH)_2 \rightleftharpoons \begin{array}{c} Cu^{++} \\ + \\ 4NH_3 \\ \upharpoonleft\downharpoonright \\ Cu(NH_3)_4^{++} \end{array} + 2OH^-$$

will shift toward the formation of the complex ion and the ion product will be decreased below that of the solubility product value; more $Cu(OH)_2$ will dissociate and the precipitate will pass into solution. The use, therefore, of a reagent which will react with a given ion to form a complex ion may be made in order to bring a substance into solution, to prevent precipitation or to remove an ion from the field of action.

16. Amphoteric Substances.—An amphoteric element is one whose hydroxide in solution ionizes both as an acid and as a base, i.e., it produces both hydrogen and hydroxyl ions. When a strong acid, such as HCl, is added to a precipitate of aluminium hydroxide (AlO_3H_3) the precipitate is dissolved and experiment shows that the aluminium is present in the solution as the positive aluminium ion (Al^{+++}). On the other hand, when a strong base, such as NaOH, is added to the aluminium hydroxide precipitate, the precipitate is dissolved; but experiment shows that the aluminium is present in the solution as negative aluminate ions (AlO_2^-). The following equilibrium is therefore assumed to exist in a neutral solution of aluminium hydroxide:

$$Al^{+++} + 3OH^- \rightleftharpoons AlO_3H_3 \rightleftharpoons H^+ + H_2AlO_3^- \rightleftharpoons H^+ + AlO_2^- + H_2O$$

When a strong acid, furnishing its high concentration of H^+, is added the above equilibrium is disturbed owing

to the union of H^+ with the OH^- present to form the very slightly ionized water. Non-ionized AlO_3H_3 then dissociates further to produce more OH^- with the final result that the aluminium hydroxide is dissolved and the aluminium remains in solution as Al^{+++}; i.e., the equilibrium shifts to the left and AlO_3H_3 acts as a base. When a strong base is added the high concentration of OH^- tends to use up the H^+ present in forming water as above. This causes a further dissociation of AlO_3H_3 to produce more H^+, with the final result that the aluminium hydroxide is dissolved and the aluminium remains in the solution as AlO_2^-; i.e., the equilibrium shifts to the right and AlO_3H_3 acts as an acid. It should be noted that if a weak base, such as NH_4OH, is substituted for the strong base mentioned above the effect will be very much less noticeable, owing to the much smaller concentration of OH^-.

17. **Oxidation and Reduction.**—When iron is acted upon by hydrochloric acid, hydrogen is displaced and iron passes into solution according to the following equation:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Considered from the ionic standpoint this gives

$$Fe + 2H^+ + 2Cl^- \rightarrow Fe^{++} + 2Cl^- + H_2$$

Now if a stream of chlorine gas is passed through the solution a further change takes place as follows:

$$Cl_2 + 2Fe^{++} + 4Cl^- \rightarrow 2Fe^{+++} + 6Cl^-.$$

In passing into solution the iron has become positively charged, while at the same time charged hydrogen has become neutral and neutral chlorine has become negatively charged.

A free atom may be said to consist of a positively charged nucleus surrounded by a number of negatively

charged particles called electrons. These electrons are capable of existing independently of the atom and hence may leave one atom and attach themselves to another. The mechanism, therefore, of the above reactions may be stated briefly as follows: An atom of iron, capable of losing electrons, comes in contact with a hydrogen ion (hydrogen atom—one electron). Two electrons leave the atom of iron and attach themselves to two hydrogen ions, which are in turn neutralized. The loss of these two electrons has, therefore, left the iron positively charged. In the second reaction a chlorine atom, capable of holding an additional electron, comes in contact with an iron ion and receives an electron from it. The chlorine, therefore, becomes negatively charged while the iron remains with a higher positive charge.

The quantity of electricity equivalent to that carried by an electron is called a "unit charge" and may be either positive or negative in character. The number of excess "unit charges" carried by an atom or ion is numerically equal to its valence. Valence, therefore, may be either a positive or a negative number depending on whether the atom or ion holds less or more electrons than is sufficient to neutralize the positive nucleus. It follows, therefore, that the valence of an element in the free state is zero and that the algebraic sum of the positive and negative valences in any compound is zero. **Oxidation consists in the loss of one or more electrons by an atom or ion,** i.e., an algebraic increase in valence. **Reduction consists in the addition of electrons to an atom or ion,** i.e., an algebraic decrease in valence. It will be seen, therefore, that oxidation and reduction must accompany each other and be equivalent in amount; i.e., in a given reaction if an element or ion loses one or more electrons those electrons must attach themselves to some other element or ion.

In writing equations of oxidation and reduction the student should first write the skeleton equation; e.g.,

when H_2S is passed into a solution of HNO_3 free sulphur is produced and the HNO_3 is reduced to nitric oxide (NO).

$$H_2S + HNO_3 \rightarrow S + NO + H_2O$$

He should then note any change in valence, i.e., what elements have lost or gained electrons during the reaction, and the number lost or gained by each atom. In the above equation sulphur has changed from a valence of negative 2 in H_2S to zero in free sulphur; i.e., each atom of sulphur has lost 2 electrons. Nitrogen, on the other hand, has changed from a positive valence of 5 in HNO_3 to positive 2 in NO; i.e., 3 electrons have attached themselves to each nitrogen atom. Since the total number of electrons lost by one element must be equal to the total number gained by the other, it is evident that 3 molecules of H_2S will furnish just enough electrons to supply those necessary to change the nitrogen in 2 molecules of HNO_3 to NO. The balanced equation, therefore, becomes

$$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$$

For purposes of balancing equations of oxidation and reduction the valence of combined hydrogen should always be considered as positive 1 and that of combined oxygen as negative 2.

A few of the more important oxidizing and reducing agents are given in the following table:

Oxidizing Agents	*Reducing Agents*
1. Halogens (Cl, Br, I)	1. $SnCl_2$
2. HNO_3	2. H_2S
3. Aqua regia	3. Nascent hydrogen
4. $KClO_4$	4. SO_2
5. Na_2O_2	5. $H_2C_2O_4$
6. $K_2Cr_2O_7$	6. Alcohol
7. $KMnO_4$	
8. PbO_2	

LABORATORY SUGGESTIONS

Qualitative Analysis has to do with both dry and wet reactions. The dry reactions are those used largely in blow-pipe analysis and will not be considered here. Since wet reactions will be used almost exclusively in this outline a brief consideration of some of the most important processes is given.

Filtration.—Since a finely divided precipitate not only tends to pass through the filter and so make its separation difficult but also tends to clog the filter paper and thus render the process of filtration slow and tedious, it is necessary to have the particles as large as possible. This is accomplished most effectively by adding the precipitating agent slowly to a hot solution. Whenever permissible, time will usually be saved by filtering a solution while hot, since hot water passes through the filter paper more rapidly than cold water.

The rate of filtration is also influenced very largely by the position of the filter paper in the funnel. The paper should fit closely against the funnel so that no air passages exist between. This may be accomplished by folding the circular filter paper in half and then folding again as shown in Fig 1. The second fold should be pinched together at the point, opened between the longer fold so as to form an inverted cone and pressed gently into the funnel until it fits snugly against the glass all the way around. Without removing it from the funnel the second fold may now be creased and the paper wet with a stream of water blown from the wash bottle to hold it in position (Fig. 2).

Wash Bottle.—After checking in his apparatus each student should make a wash bottle, using a 500 cc. or 750 cc. Florence flask. The wash bottle should be made sufficiently compact so that it can be easily held and the nozzle manipulated with one hand. A convenient form is shown in Fig. 3.

Record of Results.—The student should keep a careful and accurate record of all results obtained in his analysis

of "unknowns." The keeping of this record not only enables the student to understand the principles involved and to follow the procedures more easily, but also it often enables the instructor to determine the causes of errors and so help the student to avoid repeating them. The

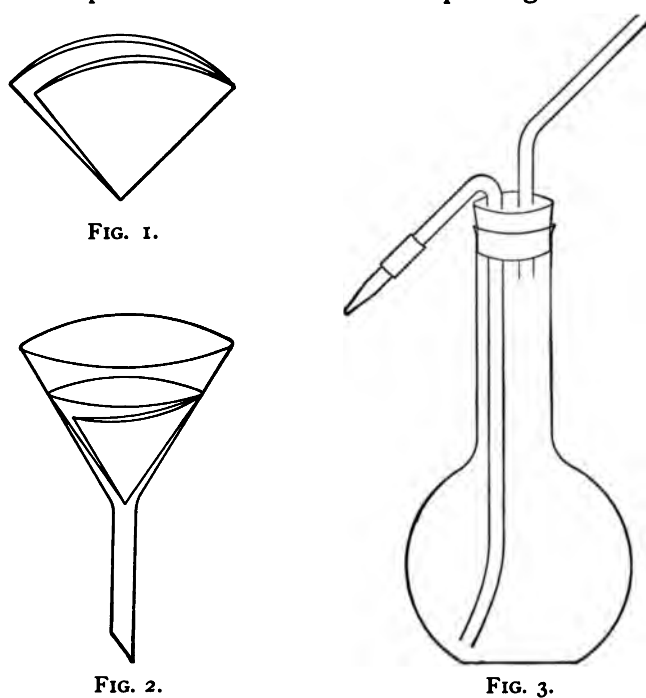


FIG. 1.

FIG. 2.

FIG. 3.

following form for "unknowns" has been found to be very easily kept and quite satisfactory:

No.	Substance	Reagent	Result	Conclusion
1	Unknown	NH_4Cl	White ppt.	Group I present
2	Ppt. 1	2N. HCl	White res.	$PbCl_2$, Hg_2Cl_2, AgCl
3	Fil. 2	H_2S	Soln.	No Bi or Sb
4	Res. 2	Hot H_2O	White res.	Hg_2Cl_2, agCl
5	Fil. 4	H_2SO_4	Soln.	No Pb
6	Res. 4	NH_4OH	Black res.	Hg present
7	Fil. 6	HNO_3	White ppt.	Ag present

The student will also find it of considerable benefit to keep a record of his results obtained in preliminary experiments by underlining and noting the color of all precipitates in outline form similar to that of Table I and the following tables.

PART II

THE SYSTEMATIC ANALYSIS

Cations—(metal ions)

Preparation of Solution

If the unknown substance is a liquid or solution treat by (1); if a solid non-alloy treat by (2) and if an alloy treat by (3).

For the purpose of a complete qualitative analysis the unknown should be divided into four parts as follows:

First part for organic matter and general information.
Second part for analysis of cations (metal ions).
Third part for analysis of anions (acid ions).
Fourth part for special tests and in case of accident.

(1) **Unknown Liquid.**—Test with litmus for acidity. Evaporate a known volume to dryness in a porcelain dish and note the amount of residue. If organic matter may be present test the residue by (4). In case organic matter is known to be absent treat an amount of the solution which contains about 1 gram of solid by (10).

(2) **Unknown Solid (non-alloy).**—Treat a small portion (about 0.1 gm.) of the finely powdered substance for organic matter by (4). If organic matter is absent add to another small portion in a test-tube 10–15 cc. of water, and shake the mixture thoroughly. If it fails to dissolve, heat to boiling. In case the substance is insoluble in water try to dissolve another small portion in 5 cc. of

6N. HNO_3. From the knowledge gained by the above tests treat about 1 gram of the solid according to (*a*), (*b*) or (*c*).

(*a*) *If the substance is soluble in water or dilute HNO_3*, dissolve about 1 gram of it using as little of the 6N. acid as possible (see Discussion 3) and treat by (10).

(*b*) *If the substance is soluble in dilute HCl*, dissolve about 1 gram. If more than 5 cc. of the 6N. HCl is used evaporate the solution to 5 cc. (see Discussion 3) dilute with water to a volume of 100 cc. and treat by (20).

(*c*) *If the substance is insoluble in dilute acid*, add to about 1 gram of the finely powdered substance in a porcelain dish 6 cc. of 12N. HCl, cover the dish with a watch glass and heat gently. (See Discussion 4.) If a residue remains, cool, add 2 cc. of 16N. HNO_3 and heat the mixture. In either case finally evaporate just to dryness, moisten the residue with 12N. HCl and again evaporate to dryness. Heat the residue to 120–130° till it is thoroughly dry, keeping the dish in motion over a small flame. Loosen the residue with the end of a glass rod, add just 5 cc. of 6N. HCl (see Discussion 3) and pulverize with the rod any large particles. Cover the dish and warm the mixture, taking care that none of the acid evaporates. Add 10 cc. of water and heat to boiling. Filter while hot, treat the filtrate by (20) and the residue by (5), (6) or (7). (See Discussion 5.)

(3) **Unknown Solid (Alloy).**—To about 0.5 gram of the finely divided material in a porcelain dish add 10 cc. of 6N. HNO_3, cover with a watch glass and warm gently as long as the action continues, adding small portions of

16N. HNO_3 from time to time if the action is renewed thereby. Finally evaporate just to dryness, add just 5 cc. of 6N. HNO_3 and 15 cc. of water. Heat to boiling, and if a residue remains, filter, treat the filtrate by (10) and the residue by (2, *c*). (See Discussion 6.)

(4) **Organic Matter.**—To determine whether organic matter is present in an unknown a small portion of the solid is placed in a hard glass test-tube or in a glass tube closed at one end and heated to dull redness. If the substance chars (a black color may be due to certain metallic oxides) and emits a burnt odor, organic matter is present and should be removed as follows (see Discussion 7). Place about 1 gram of the solid substance (more if the amount of organic matter is large) in a porcelain dish and heat gently with 5 cc. of conc. H_2SO_4 until it is well charred. Cool, add slowly and with constant stirring 16N. HNO_3 until violent action ceases. Warm gently for a few minutes and then heat more strongly, keeping the contents well stirred, until the substance is thoroughly charred. Repeat the process until the mixture becomes light straw colored and remains so when strongly heated. Treat by (*a*) or (*b*).

(*a*) *If the substance has dissolved completely*, evaporate under a hood to 1.5 cc., cool and pour the contents into 15 cc. of water. If there is a residue, heat to boiling and boil as long as it seems to be dissolving. Filter off any remaining residue, wash thoroughly and treat by (6). Treat the filtrate by (10).

(*b*) *If the substance has not dissolved completely* transfer to a platinum crucible and treat by (5), or if the platinum crucible is not available, evaporate to 1.5 cc. as in the preceding paragraph, pour the contents into 15 cc. of water, heat to boiling, filter, wash thoroughly and treat the filtrate by (10). Treat the residue by (7).

(5) **Treatment with H_2F_2.**—Transfer the residue from (2, *c*) or the mixture from (4, *b*) to a platinum crucible, add enough conc. H_2SO_4 to make a total volume of 3 cc. (see Discussion 3); heat the mixture with a moving flame until the thick white fumes of H_2SO_4 appear.

To test for silicate or silica add carefully from a loop of a platinum wire 5–6 drops of pure conc. H_2F_2 and warm the mixture over a steam bath. The formation of gas bubbles shows the presence of silica or silicate. (See Discussion 5.)

Now add 2–5 cc. more of the pure conc. H_2F_2, cover the crucible and digest the mixture on the steam bath for about fifteen minutes unless solution takes place more quickly. Remove the cover and evaporate carefully until the white fumes of H_2SO_4 appear. Treat by (*a*) or (*b*).

(*a*) *If there is no residue or precipitate* evaporate carefully to dryness. If there is still no residue, or only an insignificant one, the material contained only silica or silicate and may be discarded.

(*b*) *If there is a residue or precipitate* pour the contents of the crucible into 15 cc. of water, rinsing out the crucible with the resulting solution. Boil the mixture gently as long as any of the residue seems to dissolve. Filter and treat the filtrate by (10). Wash the residue with 1N. H_2SO_4, rejecting the washings, and treat by (7).

(6) **Treatment with Na_2CO_3 Solution.**—Mix the residue obtained in (2, *c*) or (4, *a*) with 10 parts of solid Na_2CO_3 and 20 cc. of water and boil the mixture for about five minutes. Filter and reject the filtrate (see Discussion 8). Wash the residue and dissolve it by adding 6N. HCl until the solution remains acid; then add just 5 cc. more of the acid and 10 cc. of water. Filter if necessary and treat the filtrate by (20). If there is a residue undissolved by this treatment treat it by (7).

(7) **Fusion with Na_2CO_3.**—Mix the residue from (2, *c*), (4, *b*) or (6) with ten times its weight of Na_2CO_3 in a platinum or nickel crucible (see Discussion 9) and heat over a very hot flame until complete fusion takes place. If necessary to secure a clear fusion, add 0.1–0.3 gram of $NaNO_3$ (see Discussion 10). Cool, place the crucible and contents in a dish and add carefully 6N. HCl until the solution is acid. Evaporate to dryness and heat to 120–130° to render the silica insoluble. Add just 5 cc. of 6N. HCl (see Discussion 3) and 10 cc. of water and heat to boiling. Filter to remove silica and treat the filtrate by (20).

Discussion

1. Difficultly soluble solids are more easily brought into solution if they have previously been reduced to a fine powder. This is usually done by grinding the solid in a porcelain or agate mortar. In the case of very hard substances, such as certain minerals and rocks, a heavy porcelain or iron mortar should be used to reduce them to small particles.

2. The preliminary tests with water and dilute acids should be carried out, since they furnish important indications as to the nature of the constituents present and often enable the analyst, especially the beginner, to obtain a solution more quickly and easily.

3. In order that the solution may have the proper acid concentration for the precipitation of Group II metals, just 5 cc. of 6N. acid should be present. If, therefore, the sample can be dissolved by the use of 5 cc. of 6N. acid, a considerable saving of time will be obtained.

4. A mixture of HCl and HNO_3 (3 : 1), known as aqua regia, is a very powerful oxidizing agent and is often used very effectively as a solvent. It should be used, however, only in case dilute acids or conc. HCl prove ineffective, since compounds comparatively soluble in these reagents may be rendered insoluble by its oxidizing

action; e.g., antimony and tin compounds may be oxidized to insoluble antimonic oxide (Sb_2O_5) and metastannic acid $(H_2SnO_3)_n$ respectively. The action of 12N. HCl is noted, therefore, before the HNO_3 is added.

Such substances as MnO_2 and PbO_2 are reduced and dissolved by 12N. HCl. Hot 12N. HCl slowly dissolves such oxides as Sb_2O_5, SnO_2, Fe_2O_3 and Al_2O_3. Upon the addition of conc. HNO_3, gold, platinum and HgS are dissolved. Silver compounds are changed by HCl to AgCl, somewhat soluble in concentrated acid but left almost completely in the residue on the subsequent addition of dilute HCl.

5. A residue undissolved by aqua regia may consist wholly of silica or silicates. The H_2F_2 treatment decomposes most silicates with the formation of SiF_4, a gas insoluble in conc. H_2SO_4, and hence volatilizes. The treatment is, therefore, very effective for decomposing rocks, ores or other substances which might contain silica or silicates.

The residue undissolved by H_2SO_4 may contain the sulphates of barium, lead, strontium, calcium and chromium. It may also contain bismuth as basic sulphate and antimony as Sb_2O_5 along with undecomposed AgCl.

6. Most alloys are attacked by conc. HNO_3, all of the elements present going into solution except antimony, tin, carbon and silicon. Antimony, tin and silicon are oxidized to Sb_2O_5, $(H_2SnO_3)_n$ and H_2SiO_3 respectively, all of which form white amorphous precipitates.

Certain alloys, especially those containing iron and aluminium, are more readily attacked by HCl. Treatment of the residue with HCl and aqua regia not only brings these alloys into solution but tends to dissolve the oxides of tin and antimony formed by HNO_3. The HNO_3 treatment is made first in order to remove any silver or lead which would be precipitated as chlorides if aqua regia were used.

7. Certain kinds of organic matter, such as sugars,

tartaric acid, etc., prevent the precipitation of aluminium and chromium hydroxides. Large quantities of organic matter of any kind interfere in precipitations, filtrations, etc. Therefore, if organic matter is present it should be removed before beginning the systematic analysis. Organic matter may be removed by the H_2SO_4 and HNO_3 treatment as outlined, or by ignition. The latter, however, is inadvisable in a systematic analysis since such substances as mercury and arsenic are volatilized thereby.

8. The sulphates of barium, lead, strontium, calcium and bismuth are converted into carbonates by boiling with Na_2CO_3. A second treatment is sometimes necessary to convert all the barium into the carbonate. The carbonates are readily dissolved in HCl. Anhydrous chromic sulphate is converted into the hydroxide by boiling with Na_2CO_3. The hydroxide is soluble in HCl. AgCl is only slightly attacked by the Na_2CO_3 solution.

9. Most substances are decomposed and rendered soluble by fusion with Na_2CO_3, the basic elements forming carbonates and the acidic elements forming sodium salts. In some cases, however, the carbonate is decomposed with the formation of the oxide or even the metal. For this reason care must be exercised in the use of a platinum crucible, since these metals readily alloy with the platinum. Substances which might contain any of the metals in Groups I and II should not be fused with an alkali flux in platinum. Although a nickel crucible may be used, the latter is attacked to such an extent that a subsequent test for this element or for the alkali metals is rendered unreliable.

10. The addition of $NaNO_3$ to the Na_2CO_3 fusion serves to oxidize certain substances not acted upon by the Na_2CO_3 alone. Sulphides are oxidized to sulphates, chromium compounds to chromates and manganese compounds to manganates. If the fusion is to be made in platinum the quantity of $NaNO_3$ added should be as small as possible.

Group I

Prelminary Experiments

Bi^{+++}, Sb^{+++}, Pb^{++}, Hg^{+}, Ag^{+}

In connection with the following experiments study Table I.

Experiment 1.—Introduce into separate test-tubes 5 cc. portions of the test solutions containing the above ions. Test for acidity with litmus paper and if not already acid make distinctly acid with 6N. HNO_3. In each case dilute with water to a volume of 10 cc. and add NH_4Cl as long as a precipitate continues to form. Decant, or filter if necessary, and treat the precipitates as directed in Exp. 2. Write equations.

NOTES.—Water, though very slightly ionized, reacts with salts of the less basic metals to form oxy-compounds or even acids. This reaction is called hydrolysis. The ionization of water is prevented in large measure by the presence of strong acids or strong bases. Bi and Sb are both weakly basic in character and hence tend to react with the water. This tendency is aided either by a high concentration of their salts or by a low concentration of acid. The addition of NH_4Cl as directed above, therefore, may or may not give a precipitate, since the neutral chlorides are soluble. (See Introduction 14). If hydrolysis occurs, however, the change may be considered to proceed as follows:

$$BiCl_3 \rightarrow Bi(OH)_2Cl \rightarrow \underline{BiOCl}$$

Experiment 2.—To each of the above precipitates (Exp. 1) add 5–10 cc. of cold 2N. HCl and mix thoroughly. Note the solution of BiOCl and SbOCl. (Difference, separation of Bi and Sb.) Filter off the solution from the $PbCl_2$ and saturate the filtrate with H_2S. Saturate the solutions containing Bi^{+++} and Sb^{+++} with H_2S. Write all equations.

Experiment 3.—Add to the precipitates of $PbCl_2$, Hg_2Cl_2 and AgCl (Exp. 2) 10 cc. of boiling water. Note the solution of $PbCl_2$. (Difference, separation of Pb.)

Experiment 3a.—Divide the $PbCl_2$ solution (Exp. 3) into two parts and add $K_2Cr_2O_7$ to the one and H_2SO_4 to the other. Note the color and nature of the precipitates formed. Write equations. Which of the above reagents should give the more satisfactory test for Pb^{++}.

Experiment 4.—Decant the liquid from the residues of Hg_2Cl_2 and AgCl (Exp. 3) and add NH_4OH as long as the reaction seems to continue. Note the solution of AgCl. (Difference, separation of Hg.)

NOTES.—In the presence of NH_4OH, Hg_2Cl_2 is changed by auto-oxidation to white $HgNH_2Cl$ and black, finely divided Hg. A part of the mercury in its reduction to the metallic state oxidizes the remainder to the bivalent condition. The compound $HgNH_2Cl$ may be considered to be formed from $HgCl_2$ by replacing a chlorine atom by the univalent radical (NH_2). The reaction proceeds as follows:

$$Hg_2Cl_2 + 2NH_4OH \rightarrow HgNH_2Cl + Hg + NH_4Cl + 2H_2O.$$

A solution of NH_4OH contains a considerable proportion of NH_3 molecules which unite readily with Ag^+ to form the complex ion $Ag(NH_3)_2{}^+$. Therefore, when AgCl is treated with NH_4OH the Ag^+ is removed by the formation of the complex $Ag(NH_3)_2{}^+$ which shifts the equilibrium toward the formation of more Ag^+ (Le Chatelier's Principle) with the result that the AgCl is dissolved. The reaction proceeds as follows:

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2Cl$$

Experiment 5.—Acidify the solution of $Ag(NH_3)_2Cl$ (Exp. 4) with HNO_3. A white precipitate of AgCl is obtained, owing to the removal of NH_3 in the reversible action above.

TABLE I

Outline for the Systematic Separation and Detection of Group I

Ions present in acid solution

Reagent	Bi^{+++}	Sb^{+++}	Pb^{++}	Hg^{+}	Ag^{+}
1 NH_4Cl	BiOCl (?)	SbOCl (?)	$PbCl_2$	Hg_2Cl_2	AgCl
2 HCl(2N)	$BiCl_3$	$SbCl_3$	$PbCl_2$	Hg_2Cl_2	AgCl
H_2S	B_2iS_3 *	Sb_2S_3 *	↓	↓	↓
3 H_2O (Hot)	↓	↓	$PbCl_2$	Hg_2Cl_2	AgCl
(a) $K_2Cr_2O_7$			(a) $PbCrO_4$	↓	↓
(b) H_2SO_4			(b) $PbSO_4$		
4 NH_4OH			↓	$HgNH_2Cl+Hg$	$Ag(NH_3)_2Cl$
5 HnO_3				↓	AgCl

* May be added to Group II ppt. or tested according to method outlined in Group II.

Analysis

Group I

Bi^{+++}, Sb^{+++}, Pb^{++}, Hg^{+}, Ag^{+}

(10) **Precipitation.**—To about 25 cc. of the solution of the substance acidified with HNO_3 (see Discussion 11) add NH_4Cl solution as long as a precipitate continues to form. Mix thoroughly and allow the mixture to stand for two or three minutes. Filter and treat the precipitate by (11). Reserve the filtrate for analysis of Group II. (20).

(11) **Separation of Bismuth and Antimony.**—Pour repeatedly through the filter (10) a cold 10 cc. portion of 2N. HCl. Treat the residue by (12). Dilute the filtrate with an equal volume of water and saturate with H_2S. A brown precipitate indicates the presence of bismuth. An orange-red precipitate indicates the presence of antimony and the absence of bismuth. Confirmatory tests may be made according to the methods outlined in Group II, or the precipitate may be added to that of the Group II sulphide (20) and analyzed according to the general scheme.

(12) **Separation and Detection of Lead.**—Pour repeatedly through the filter (11) a 10 cc. portion of boiling

water. Cool, acidify with $HC_2H_3O_2$ and add a slight excess of $K_2Cr_2O_7$ solution. The formation of a yellow crystalline precipitate shows the presence of lead. If lead has been found, wash the residue left by the hot water, and treat it by (13). (See Discussion 14.)

(13) **Detection of Mercury.**—Pour repeatedly through the filter (12) a 5–10 cc. portion of NH_4OH. A black residue left on the filter paper shows the presence of mercury. Treat the filtrate by (14).

(14) **Detection of Ag.**—Acidify the filtrate (13) with HNO_3. The formation of a white curdy precipitate undissolved by the HNO_3 shows the presence of Ag. (See Discussion 15.)

Discussion

11. The chlorides of lead, silver and mercury (ous) are insoluble in acid of moderate concentration but tend to redissolve in strongly acid solutions, owing to the formation of complex ions such as $AgCl_2^-$. If the solution to be tested is strongly acid with an unknown acid it should be nearly neutralized with NH_4OH before the addition of NH_4Cl. Complete neutralization causes the precipitation of metal hydroxides and oxy-compounds which may not readily dissolve on the subsequent addition of acid. It is preferable, therefore, not to completely neutralize at this time.

12. Owing to the rather high solubility product of $PbCl_2$ it is often incompletely precipitated in Group I. Its solubility, however, is considerably lessened by the addition of a large excess of NH_4Cl because of the common ion effect. The mass-law equation representing the solubility product of $PbCl_2$ is $C_{Pb^{++}} \cdot C^2_{Cl^-} = \mathbf{K}$. Since the product of the concentrations of its ions must under all conditions have a definite value it is readily seen that an increase of Cl^- must result in a decrease of Pb^{++}. The Pb^{++}, however, can decrease only by forming non-ionized $PbCl_2$, and if the solution is saturated with respect to

$PbCl_2$ molecules, precipitation must take place. The reaction may be represented by the following equilibrium:

$$\underline{PbCl_2} \rightleftharpoons PbCl_2 \rightleftharpoons Pb^{++} + 2Cl^-$$

13. As was pointed out in the preliminary experiments, the precipitation of bismuth and antimony in this group is due to hydrolysis. Application of the Law of Mass Action to this reaction shows that their precipitation may be practically or wholly prevented not only by an excess of acid but also by an excess of chloride ion. For the solubility product of BiOCl we have the expression $C_{Bi^{+++}} \cdot C_{O^{--}} \cdot C_{Cl^-} = \mathbf{K}$. The excess of H^+ from the acid unites with the O^{--} to form the very slightly ionized H_2O and so reduces the concentration of O^{--}. This in turn tends to reduce the ion product and hence causes the Bi to remain in solution. An excess of Cl^- would tend to shift the equilibrium toward the formation of non-ionized $BiCl_3$ and so reduce the concentration of Bi^{+++}. The result again is to reduce the ion product and prevent precipitation. The same reasoning applies to the formation of SbOCl. (The student should make the application.)

14. The solvent action of hot water on $PbCl_2$ is somewhat slow, hence the necessity of pouring the water repeatedly through the filter containing the mixed chlorides. Any undissolved $PbCl_2$ left on the filter may react with the NH_4OH, subsequently added for the separation of mercury and silver, to form a basic chloride, PbOHCl. This causes a turbidity in the filtrate containing the dissolved silver. The presence of this, however, does not interfere with the test for silver, since it is readily dissolved by the HNO_3.

15. The presence of a large quantity of mercury renders the test for silver less delicate, owing to the reducing action of free mercury on the silver salt.

$$Hg + 2AgCl \rightarrow HgCl_2 + 2Ag$$

The silver thus reduced is insoluble in NH_4OH and

is, therefore, left in the residue mixed with the $HgNH_2Cl$ and free mercury. In case the quantity of silver is relatively small as compared to the mercury it might be completely reduced and hence remain in the residue. If a heavy black residue is obtained on the addition of NH_4OH and silver is not found in the filtrate, the residue should be tested for silver as follows: Dissolve the residue in a small quantity of aqua regia, dilute with water and filter off the dissolved mercury. Leach the residue with NH_4OH to dissolve any AgCl, and test the filtrate for silver as outlined in Analysis (14).

Group II

Preliminary Experiments

Group II, Copper Division

Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}

In connection with the following experiments study Tables II and III.

Experiment 6.—Dilute separate 5 cc. portions of each of the test solutions containing the above ions with an equal volume of water and saturate with H_2S. Allow the precipitates to settle; then decant off the supernatant liquid (filter if necessary) and wash each of the precipitates by decantation with about 10 cc. of water in order to remove the remaining acid. Write equations.

Experiment 7.—To each of the above precipitates (Exp. 6) add 10 cc. of 2N. HNO_3 and heat to boiling. Note the insolubility of HgS. (Difference, separation of Hg.) Write equations.

NOTE.—If too strong HNO_3 is added or if the boiling is long continued the HgS is largely converted into a white difficultly soluble substance of the probable formula $2HgS \cdot Hg(NO_3)_2$ while some may be completely dissolved as $Hg(NO_3)_2$.

Experiment 7a.—Pour off the liquid above the residue of HgS (Exp. 7) and add 5 cc. of aqua regia (3 parts of $12N \cdot HCl$ to 1 part of $16N \cdot HNO_3$) and warm gently until solution is complete. Evaporate almost to dryness, add 5–10 cc. of water and then stannous chloride ($SnCl_2$) drop by drop. Write equations.

NOTES.—The failure of the HgS to dissolve in $2N. HNO_3$ is due not only to the small number of its ions in a saturated solution but also to the slow removal of the sulphide ion by oxidation with the dilute HNO_3. Aqua regia is a much stronger oxidizing agent. It readily oxidizes the sulphide ion and so brings the mercury into solution.

$HgCl_2$ is reduced to white Hg_2Cl_2 by the action of $SnCl_2$. This is then further reduced to free Hg by an excess of $SnCl_2$, hence the change in color from white to gray.

Experiment 8.—To each of the solutions containing Pb^{++}, Bi^{+++}, Cu^{++}, and Cd^{++} (Exp. 7) add 1 cc. conc. H_2SO_4 and evaporate until the white fumes of SO_3 begin to appear. Cool and add 10 cc. of water. Note the fact that $PbSO_4$ remains insoluble. (Difference, separation of Pb.) Write equations.

NOTES.—$PbSO_4$ is somewhat soluble in HNO_3. In order to effect a complete precipitation of lead it is necessary to remove the HNO_3. This may be done by evaporation since the boiling-point of HNO_3 (120.5°) is so much lower than that of the H_2SO_4 (338°). The appearance of the white fumes of SO_3 is evidence of the complete removal of HNO_3.

$Bi_2(SO_4)_3$ ordinarily dissolves on the addition of water but if much bismuth is present a coarsely crystalline precipitate of $(BiO)_2SO_4$ may separate out slowly when cold, and more quickly when heated.

Experiment 8a.—Decant or filter off the clear liquid from the insoluble $PbSO_4$ and dissolve it by shaking with 10 cc. of ammonium acetate ($NH_4C_2H_3O_2$). Acidify the solution with $HC_2H_3O_2$ and add a few drops of $K_2Cr_2O_7$. The precipitate is $PbCrO_4$. Write equations.

NOTE.—$PbSO_4$ is soluble in $NH_4C_2H_3O_2$ owing to the formation of the very slightly ionized $Pb(C_2H_3O_2)_2$. It should be remembered that most salts are highly ionized. (See table, Introduction, 9.)

Experiment 9.—To each of the solutions containing Bi^{+++}, Cu^{++}, and Cd^{++} (Exp. 8) slowly add NH_4OH to distinctly alkaline reaction. Note the formation of a permanent white precipitate of BiOOH. The precipitates of $Cu(OH)_2$ and $Cd(OH)_2$ redissolve on the addition of an excess of the reagent. (Difference, separation of Bi.) Write equations.

NOTE.—According to the Law of Mass Action the limit of solubility of any acid, base or salt is reached when the product of the concentration of its ions equals a certain maximum, called the solubility product. (Conc. of pos. ions × Conc. of neg. ions = a const., solubility product.) If NH_4OH is added to a bismuth salt, precipitation of BiOOH begins when enough OH^- have been added to reach the solubility product for BiOOH. The greater the concentration of OH^-, i.e., the greater the excess of NH_4OH, the smaller must be the concentration of the Bi^{+++} and hence the more complete the precipitation. It will be recalled, however, that an addition of an excess of NH_4OH dissolves both $Cu(OH)_2$ and $Cd(OH)_2$. This is explained by the fact that the Cu^{++} and Cd^{++} unite with HN_3 to form the complex ions $Cu(NH_3)_4{}^{++}$ and $Cd(NH_3)_4{}^{++}$ (See Introduction 15.) This removes the Cu^{++} and Cd^{++} as such and prevents their precipitation. The Bi^{+++}, incapable of forming a complex ion with NH_3, must be removed by precipitation as indicated above.

Experiment 9a.—Decant or filter off the clear liquid from the precipitate of BiOOH and dissolve it in a few cc. of 6N. HCl. Evaporate to about 1 cc. and pour into a large volume of warm water. Filter off the white milky precipitate of BiOCl and pour over the precipitate on the filter paper a freshly prepared solution of sodium stannite (Na_2SnO_2). (See Appendix 1.) The black residue is finely divided bismuth. Write equations.

NOTE.—The solution of $BiCl_3$ is evaporated to remove the excess of HCl in order to promote hydrolysis. (See Preliminary Exp. 1, also Introduction, 14.)

Experiment 10.—Divide each of the solutions containing copper and cadmium (Exp. 9) into two parts. Acidify

the first portion of each with $HC_2H_3O_2$ and add a few drops of $K_4Fe(CN)_6$. Note the color of the precipitates formed. (Difference, detection of Cu.) Write equations.

To the second portion containing copper add KCN (**Care, Poison**) until the blue color just disappears; then add an equal volume to the second portion containing cadmium. Saturate each with H_2S. Note the formation of insoluble CdS. (Difference, detection of Cd.)

NOTE.—Excess KCN reacts with salts of copper and cadmium to form the complex ions $Cu(CN)_2^{++}$ and $Cd(CN)_4^{++}$. The $Cu(CN)_4^{++}$ first formed immediately decomposes into $Cu(CN)_2^{+}$ and C_2N_2. The C_2N_2 reacts with NH_4OH to form NH_4CNO and other more or less complex substances. The failure to obtain a precipitate with H_2S is evidence that not enough Cu^{+} or Cu^{++} is present to reach the solubility product for Cu_2S or CuS and shows that the complex ion $Cu(CN)_2^{+}$ is only very slightly dissociated. On the other hand, the complex ion $Cd(CN)_4^{++}$ must be dissociated to a considerable extent since it produces sufficient Cd^{++} to reach the solubility product for CdS. The reactions proceed as follows:

$$2Cu(NH_3)_4SO_4 + 4KCN \rightarrow 2KCu(CN)_2 + C_2N_2 + 4NH_3 + K_2SO_4$$

$$Cd(NH_3)_4SO_4 + 4KCN \rightarrow K_2Cd(CN)_4 + 4NH_3 + K_2SO_4$$

TABLE II

OUTLINE FOR THE SYSTEMATIC SEPARATION OF GROUP II
(SEPARATION INTO CU AND SN DIVISIONS)
Ions present in 0.3N. HCl solution

No.	Reagent	Hg^{++}	Pb^{++}	Bi^{+++}	Cu^{++}	Cd^{++}	As^{+++} or As^{+++++}	Sb^{+++}	Sn^{++} or Sn^{++++}
1	H_2S	HgS	PbS	Bi_2S_3	CuS	CdS	As_2S_3 As_2S_5	Sb_2S_3	SnS or SnS_2
2	$(NH_4)_2S_x$	HgS	PbS	Bi_2S_3	CuS	CdS	$(NH_4)_3AsS_4$	$(NH_4)_3SbS_4$	$(NH_4)_2SnS_3$
3	6N. HCl	↓	↓	↓	↓	↓	As_2S_5	Sb_2S_5	SnS_2
							↓	↓	↓

ANALYSIS

Group II

Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++},
As^{+++}, As^{+++++}, Sb^{+++}, Sn^{++}, Sn^{++++}

(20) **Precipitation.** — Dilute the filtrate (10) which should contain just 5 cc. of 6N. acid (see Discussion 16) to 100 cc. and saturate with H_2S. Filter, heat the filtrate to boiling and again saturate with H_2S.

If no further precipitate forms reserve the solution for analysis of Group III (50) and treat the precipitate by (21).

If a further precipitate forms (see Discussion 17) evaporate the mixture to dryness, moisten the residue with conc. HCl and evaporate to dryness again to remove all HNO_3. Add 10–15 cc. of 6N. HCl, heat to boiling and pass H_2S into it for five to ten minutes. Filter, unite the precipitate to that above and treat by (30). Reserve the filtrate for analysis of Group III (50).

(21) **Separation of the Copper and Tin Divisions.**— Transfer the precipitate (20) to an evaporating dish, add 10–15 cc. of $(NH_4)_2S_x$ reagent, cover the dish with a watch glass and warm the mixture for about five minutes. (*Do not boil.*) (See Discussion 18.) Dilute with an equal

volume of water and filter. A second treatment with $(NH_4)_2S_x$ reagent should be made if the residue is large and much was extracted by the first treatment. Wash the residue with hot water (see Introduction 3, *f*) and treat it by (30). Treat the filtrates separately by (22).

(22) **Precipitation of the Tin Division.**—To the first filtrate obtained on treating the Group II sulphides with $(NH_4)_2S_x$ reagent (21) add 6N. HCl with frequent stirring until the solution remains milk-white from the separation of finely divided sulphur. Allow the mixture to stand for one or two minutes to coagulate the precipitate. The presence of the tin division is indicated by the presence of a flocculent yellow or orange precipitate. (See Discussion 19.) Treat the second filtrate obtained in (21) in the same way, and if a flocculent precipitate forms, unite it with the one obtained above. Filter and wash the precipitate, using suction to dry it as thoroughly as possible. (See Discussion 20.) Reject the filtrate and treat the precipitate by (40).

Discussion

16. The precipitation of the sulphides of the metals of both Groups II and III is determined very largely by the acid concentration of the solution. From the standpoint of the Law of Mass Action and the Ionic Theory two factors must be taken into consideration in the precipitation of the metal sulphides, viz., the value of the solubility product and the concentration of the sulphide ion. The solubility product varies with the nature of the sulphide and with the temperature. The order of precipitation with H_2S from cold HCl solution of decreasing acid concentration is about as follows: $As^{\overset{+++}{++}}$, $As^{\overset{++}{+}}$, Hg^{++}, Cu^{++}, $Sb^{\overset{++}{+}}$, $Bi^{\overset{++}{+}}$ and $Sn^{\overset{++}{++}}$, Cd^{++}, Pb^{++} and Sn^{++}, Zn^{++}, Fe^{++}, Ni^{++}, Co^{++}, Mn^{++}.

According to Henry's Law of the Solubility of Gases, the solubility and therefore the concentration of H_2S will have a constant value at a definite temperature and

pressure. H_2S ionizes to a slight extent into H^+ and HS^- and to a much less extent into $2H^+$ and $S^=$. Since the $S^=$ is the active agent in the precipitation under discussion only the latter ionization need be considered here.

The expression of the Law of Mass Action for H_2S is

$$\frac{C^2_{H^+} \cdot C_{S^=}}{C_{H_2S}} = K$$

In a saturated solution, however, C_{H_2S} is a constant; hence simplifying the above equation gives

$$C^2_{H^+} \cdot C_{S^=} = K \cdot C_{H_2S} = \mathbf{K}$$

From this it is readily seen that any increase in the concentration of H^+ must result in a corresponding decrease in $S^=$. But in order that a sulphide, e.g., CdS, may precipitate, its solubility product, $C_{Cd^{++}} \cdot C_{S^=} = \mathbf{K}_{CdS}$, must be reached. Therefore, if the acid concentration is large the concentration of $S^=$ may become so small that its product with $C_{Cd^{++}}$ will not equal the solubility product for CdS. On the other hand, if the acid concentration is small the concentration of $S^=$ may become so large that its product with $C_{Zn^{++}}$ will equal the solubility product for ZnS, in which case ZnS would be precipitated in Group II. In order to make a complete separation between Groups II and III, the concentration of $S^=$ must be so regulated that there will be sufficient to reach the solubility product of the most soluble of the sulphides of Group II but not sufficient to reach the solubility product of the least soluble of Group III. (See table, Introduction 11). The necessity of following the directions very accurately is therefore evident.

17. When H_2S is passed into a cold acid solution containing an arsenate, reaction takes place only very slowly between the two substances. Part of the arsenic is precipitated as As_2S_5 and a part is reduced to the trivalent state and precipitated as As_2S_3. When the solution is heated the reduction takes place somewhat more rapidly. The most favorable conditions for the reduction and pre-

cipitation of arsenates with H_2S is from a hot solution having a comparatively high concentration of acid.

18. In the separation of arsenic, antimony and tin from the copper division, advantage is taken of the acid character of the elements of the tin division and their ability to form sulpho-salts with $(NH_4)_2S_x$. This reagent, however, has a slight solvent action on the sulphides of copper and mercury. If $(NH_4)_2S_x$, to which about 5 per cent NaOH has been added, is used, the solvent action on the sulphides of copper and mercury is very much reduced and a more satisfactory separation is obtained. Excessive heat not only increases the solvent action on HgS and CuS but decomposes the reagent with precipitation of free sulphur.

19. If the separation of arsenic, antimony and tin from the copper division has been complete the presence of the tin division is shown by a flocculent yellow or orange precipitate on acidification of the $(NH_4)_2S_x$ solution with HCl. However, if the precipitate obtained is brown (indicating copper) dark gray (indicating mercury), or of unpronounced yellow or orange, so as to make doubtful the presence of the tin division, much time can often be saved by proceeding as directed below. Small amounts of copper which otherwise might be overlooked may also be detected.

Heat the precipitate with 10–20 cc. of NH_4OH almost to boiling for five minutes, and filter. This treatment dissolves all but the copper and free sulphur. The residue, therefore, should be tested for copper according to (31) (34) and (36) unless copper has already been found. Pass H_2S into the filtrate for fifteen to twenty seconds to precipitate any HgS and change the partially sulphurated acids $(NH_4)_3AsO_3S$, $(NH_4)_3AsO_2S_2$, etc., into the fully sulphurated form $(NH_4)_3AsS_4$, etc. Filter if necessary and acidify the filtrate with HCl. Filter off the precipitated sulphides, wash, dry by suction and treat by (40).

20. If a suction pump is not available the precipitate may be dried satisfactorily by pressing the filter containing it between several thicknesses of clean filter paper.

TABLE III

Outline of the Systematic Separation and Detection of Group II (Cu Division)

No.	Reagent	HgS	PbS	Bi_2S_3	CuS	CdS
1	2N. HNO_3	$\underline{HgS}$	$Pb(NO_3)_2$	$Bi(NO_3)_3$	$Cu(NO_3)_2$	$Cd(NO_3)_2$
	Aqua regia	$HgCl_2$	↓	↓	↓	↓
	$SnCl_2$	$\underline{Hg_2Cl_2}$ $\underline{Hg}$				
2	Conc. H_2SO_4 $NH_4C_2H_3O_2$	↓	$\underline{PbSO_4}$	$Bi_2(SO_4)_3$	$CuSO_4$	$CdSO_4$
			$Pb(C_2H_3O_2)_2$	↓	↓	↓
	$HC_2H_3O_2$ $K_2Cr_2O_7$		$\underline{PbCrO_4}$			
3	NH_4OH		↓	$\underline{BiOOH}$	$Cu(NH_3)_4SO_4$	$Cd(NH_3)_4SO_4$
	HCl			$BiCl_3$	↓	↓
	H_2O			$\underline{BiOCl}$		
	Na_2SnO_2			$\underline{Bi}$		
4	(a) $HC_2H_3O_2$ $K_4Fe(CN)_6$			↓	$\underline{Cu_2Fe(CN)_6}$	$\underline{Cd_2Fe(CN)_6}$
	b) KCN H_2S				$KCu(CN)_2$ $KCu(CN)_2$	$K_2Cd(CN)_4$ $\underline{CdS}$

Analysis

Group II, Cu Division

(30) **Separation of Mercury.**—Transfer the residue (21) to a porcelain dish and add 10–20 cc. of 2N. HNO_3 and heat to boiling. Boil gently for two to three minutes, not longer. (See note, Preliminary Exp. 7). Filter, wash the residue and treat it by (31). Treat the filtrate by (32).

(31) **Confirmatory Test for Mercury.**—Transfer the residue (30) undissolved by HNO_3 to a porcelain dish and add 5–10 cc. of aqua regia (see Preliminary Exp. 7a). Warm gently till solution is complete, then evaporate almost to dryness, dilute with 5–10 cc. of water, filter and add to the clear filtrate some $SnCl_2$ solution, at first 1–2 drops then 2–3 cc. (see Discussion 22). The formation of a white precipitate which turns gray on the addition of excess $SnCl_2$ shows the presence of mercury. (See Discussion 23.)

(32) **Separation of Lead.**—To the filtrate obtained in (31) add 2–3 cc. of conc. H_2SO_4, transfer to a porcelain dish and evaporate until the dense white fumes of SO_3 appear. Cool, pour the mixture into a small beaker containing 10–15 cc. of water and rinse out the vessel with a portion of the solution formed, in order to be sure that all of the solid is transferred. Allow the mixture to stand four to five minutes. The formation of a fine, white, crystalline precipitate indicates the presence of lead. The precipitate may be more readily distinguished if the liquid is given a slight whirling motion, so that the precipitate will collect on the bottom of the beaker toward the center. Filter, treat the precipitate by (33) and the filtrate by (34).

(33) **Confirmatory Test for Lead.**—Dissolve the precipitate of $PbSO_4$ (32) by pouring a 10–20 cc. portion of ammonium acetate ($NH_4C_2H_3O_2$) solution repeatedly through the filter. To the filtrate add a few drops of

$K_2Cr_2O_7$ and 3–5 cc. of $HC_2H_3O_2$. A yellow precipitate is $PbCrO_4$ (see Discussion 24).

(34) **Separation of Bismuth.**—To the filtrate obtained in (32) add NH_4OH until, after shaking, a distinctly alkaline reaction is obtained. (Test with litmus.) Shake to coagulate the precipitate of BiOOH, and filter. Wash the precipitate and treat it by (35). Treat the filtrate by (36).

(35) **Confirmatory Test for Bismuth.**—Pour through the filter containing the precipitate of BiOOH (34) a cold freshly prepared solution of Na_2SnO_2 (see Appendix I). The formation of a black residue shows the presence of bismuth. (See Discussion 25.)

(36) **Detection of Copper.**—If the filtrate from the BiOOH (34) is deep blue, copper is shown to be present. If, however, it is colorless or nearly so, about one-fourth of the solution should be acidified with $HC_2H_3O_2$ and a few drops of $K_4Fe(CN)_6$ added. The formation of a red precipitate or coloration shows the presence of copper. Treat the remainder of the solution by (37) or (38.)

(37) **Detection of Cadmium.**—To the remainder of the NH_4OH solution obtained in (36) add KCN solution (*care, poison*) until the blue color just disappears; if the solution is colorless add only a few drops. Pass H_2S into the colorless solution for about half a minute. The formation of an immediate yellow precipitate (see Discussion 26) shows the presence of cadmium.

(38) **Optional Method for the Detection of Cadmium.**—Acidify the remainder of the NH_4OH solution (36) with H_2SO_4, add a few iron nails or some iron filings and boil for a short time. Filter, and unless the solution is still acid make it just acid with $6N.H_2SO_4$ and pass H_2S into it. The formation of a yellow precipitate shows the presence of cadmium.

Discussion

21. If the elements of the copper division are present in large quantity, small quantities of tin may remain

undissolved by the $(NH_4)_2S_x$ treatment. This may also occur when small quantities of cadmium and stannous tin are present together. Any tin sulphide, either SnS or SnS_2, remaining in the copper division, will be converted by the HNO_3 (30) into insoluble metastannic acid, H_2SnO_3. This is practically unaffected by the aqua regia or bromine water used in (31).

In order to recover any tin that may be left in the copper division the residue obtained by treatment with aqua regia (31) should be treated as follows: If it is dark-colored, showing incomplete removal of HgS, digest with bromine water in order completely to remove the HgS, filter and dissolve the residue in a small quantityof $(NH_4)_2S_x$ reagent. Dilute, filter if necessary, and add the solution to the main ammonium sulphide solution obtained in (21).

22. The addition of $SnCl_2$ to a solution of $HgCl_2$ causes an immediate reduction to the white Hg_2Cl_2. Further addition of $SnCl_2$ carries the reduction to free mercury, which imparts a gray appearance to the precipitate. The latter reduction is hindered very materially and may be almost prevented if excess aqua regia has not been completely removed before making the test. Bromine water may be used in place of the aqua regia. Excess bromine, however, must be removed before the addition of $SnCl_2$.

23. If the separation of mercury is incomplete and a large amount of CuS is left undissolved by the HNO_3 treatment (30), a white precipitate of CuCl will separate out on the addition of $SnCl_2$. This, however, does not turn gray with excess $SnCl_2$.

24. The confirmatory test for lead should always be made, since a precipitate with H_2SO_4 may consist of $(BiO)_2SO_4$ or $BaSO_4$. The $(BiO)_2SO_4$ is coarsely crystalline, dissolves in $NH_4C_2H_3O_2$ and gives a yellow color with $K_2Cr_2O_7$. The precipitate, however, differs from $PbCrO_4$ in that it dissolves readily in $HC_2H_3O_2$. The

$BaSO_4$ resembles $PbSO_4$ in appearance but is insoluble in $NH_4C_2H_3O_2$.

25. If, owing to occlusion or incomplete washing of the H_2S precipitate, an incomplete separation from Group III is obtained, the addition of NH_4OH for the separation of bismuth will cause the precipitation of $Fe(OH)_3$ or other hydroxides of Group III. These differ from BiOOH in that none of them are reduced by Na_2SnO_2 by short contact in the cold.

26. An immediate yellow precipitate with H_2S shows the presence of cadmium. When much copper is present and the solution is saturated with H_2S a deep yellow color soon develops and an orange-red precipitate of $(CSNH_2)_2$ may separate out on standing, owing to a reaction between the H_2S and C_2N_2 set free by the reduction of $Cu(CN)_2$.

27. If, owing to previous errors in analysis, a black precipitate (due to HgS, PbS, etc.) is obtained in the final test for cadmium with H_2S, it should be thoroughly washed and the cadmium dissolved out by boiling the precipitate with 15 cc. of 1.2N. H_2SO_4 and filtering. After it has been diluted with two to three times its volume of water the CdS if present may be precipitated by saturating with H_2S.

Preliminary Experiments

Group II, Tin Division

$$As^{+++},\ As^{+++++},\ Sb^{+++},\ Sn^{++},\ Sn^{++++}$$

In connection with the following experiments study Tables II and IV.

Experiment 11.—Dilute separate 5-cc. portions of the test solutions of each of the above ions with an equal volume of water, and saturate cold with H_2S. If a precipitate does not form heat to boiling and saturate again with

H_2S. Note the difference in action between As^{+++} and As^{+++++}. Write equations.

Experiment 12.—Decant or filter the liquid from the precipitates (Exp. 11) and dissolve each, by warming if necessary, with about 5 cc. of $(NH_4)_2S_x$ reagent. *Do NOT boil.*

NOTES.—The solubility of the sulphides of arsenic, antimony and tin is doubtless due to their acidic character and tendency to form sulpho-salts. This is in direct contrast to the metals of the copper division of Group II in that the latter are all basic in character and have very little tendency to form sulpho-salts.

The use of $(NH_4)_2S_x$ instead of $(NH_2)_4S$ is made necessary only in the cases of Sb_2S_3 and SnS. Antimony and tin must be oxidized to the higher valence since the sulpho-salt of the lower valence is apparently incapable of existence. The following reactions for the solution of As_2S_3 and As_2S_5 are as follows:

$$As_2S_3 + 6(NH_4)_2S_x \rightarrow 2(NH_4)_3AsS_4 + (6x-5)S$$

$$As_2S_5 + 6(NH_4)_2S_x \rightarrow 2(NH_4)_3AsS_4 + (6x-3)S$$

Write the corresponding equations for the solution of Sb_2S_3, SnS and SnS_2 noting the fact that in the sulpho-salt arsenic and antimony are quinquivalent while tin is quadrivalent.

Experiment 13.—Since the two solutions of arsenic are now identical, $(NH_4)_2AsS_4$, as are also those of tin, $(NH_4)_2SnS_3$, one of each may be discarded. Dilute the remaining solutions of arsenic, antimony and tin (Exp. 12) with an equal volume of water and acidify with 6N. HCl. Note the precipitate formed in each case. Write equations.

NOTE.—When $(NH_4)_2S_x$ is treated with an acid, considerable sulphur is apt to be set free. This gives a white, milky appearance to the mixture and may prevent the detection of small amounts of the sulphides. Dilution with water obviates this difficulty to some extent.

Experiment 14.—To each of the precipitates of As_2S_5, Sb_2S_5 and SnS_2 (Exp. 13) dried by suction or by pressing

between filter paper, add just 10 cc. of 12N. HCl. Place the test-tubes containing the mixtures in a beaker of water and heat to boiling. Boil gently for ten minutes. Note the solution of Sb_2S_5 and SnS_2. (Difference, separation of As.) Write equations.

NOTES.—If the boiling is carried out so that the bubbles rise but slowly from the solutions, practically no As_2S_5 is dissolved. However, if the boiling is too vigorous some of the arsenic may go into solution. This is due to removal of H_2S and consequent shifting of equilibrium.

Sb_2S_5 dissolves in 12N. HCl somewhat slowly, especially when large amounts are present. It dissolves with the formation of $SbCl_3$, the antimony being reduced by the H_2S to the trivalent condition.

Experiment 14a.—Without filtering, add small particles of $KClO_3$ or $NaClO_3$, a few at a time, to the As_2S_5 and stir till solution is complete. Evaporate to 1–2 cc. Make distinctly alkaline with NH_4OH and add 1–2 cc. of magnesia mixture ($MgCl_2$–NH_4Cl–NH_4OH). If no precipitate forms add about one-fourth its volume of NH_4OH and rub the inside of the tube with a glass rod to hasten precipitation.

NOTE.—The action of HCl on $KClO_3$ or $NaClO_3$ is to liberate chlorine and ClO_2, which remove the S = by oxidation, causing the arsenic to go into solution. It is dissolved as H_3AsO_4 instead of $AsCl_5$, very little of which remains as such even in very concentrated HCl.

$MgNH_4AsO_4$ is somewhat soluble even in cold water; therefore it is necessary to have a rather concentrated solution. It also has a tendency to hydrolize into NH_4OH and $MgHAsO_4$, a soluble salt. This tendency is counteracted by the addition of a large excess of NH_4OH. It has another peculiarity, which is not uncommon, in that it is inclined to supersaturate. This may be overcome and precipitation effected, by vigorous shaking, or by producing a rough surface in contact with the liquid.

Experiment 15.—Dilute the solutions of antimony and tin (Exp. 14) to 50 cc. and transfer one-third of each to a third vessel. Heat the remaining portions to 90° and saturate with H_2S. Note the precipitation of Sb_2S_3. (Difference, separation of Sb.) Write equations.

Experiment 15a.—Dilute the solution in the third

vessel (Exp. 15) to 50 cc. and saturate with H_2S. Note the color of the precipitate. Without filtering, boil to expel H_2S. Add bromine water and heat till solution is complete, then add 5 gms. of solid oxalic acid ($H_2C_2O_4$) and saturate with H_2S. Note the precipitation of Sb_2S_3. (Difference, separation of Sb.) Write equations.

NOTES.—There is enough difference in the solubility products of Sb_2S_3 and SnS_2 for the careful worker to make a complete separation of antimony and tin according to Exp. 15. However, if the directions for temperature and acid concentration are not carefully observed, a precipitate containing both antimony and tin may be obtained (Exp. 15*a*), in which case the separation can be made according to Exp. 15*a*.

The bromine water is used to oxidize the $S^=$ and so hasten the solution. The same results may be obtained more slowly by evaporation to concentrate the acid.

The failure of SnS_2 to precipitate in the presence of a large excess of $H_2C_2O_4$ is doubtless due to the formation of a complex which reduces the concentration of Sn^{++++}.

Experiment 16.—Dilute the solution containing tin (Exp. 15) to 50 cc. and saturate cold with H_2S. Note the precipitation of SnS_2. Without filtering, add 1–2 gms. of granulated test lead and boil two to three minutes. Cool and filter, allowing the filtrate to run into a solution of $HgCl_2$. The precipitate is Hg_2Cl_2+Hg.

NOTE.—The action of lead is to reduce the Sn^{++++} to Sn^{++}, which in turn will reduce $HgCl_2$ to Hg_2Cl_2 or even to free mercury. Stannic tin has no effect on $HgCl_2$; hence the necessity for reduction before the final test.

TABLE IV

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP II (SN DIVISION)

No.	Reagent	As_2S_5	Sb_2S_5	SnS_2
1	12N. HCl	As_2S_5	$SbCl_3$	$SnCl_4$
	HCl			
	$KClO_3$	H_3AsO_4		
	Magnesia mixture	$MgNH_4AsO_4$		
	6N. HCl	H_3AsO_4	↓	↓
	H_2S	As_2S_{3-5}		
2	H_2S		Sb_2S_3	$SnCl_4$
3	HCl − Br_2		$SbCl_3$	$SnCl_4$
4	$H_2C_2O_4$	↓		
	H_2S		Sb_2S_3	
5	Pb			$SnCl_2$
6	$HgCl_2$		↓	$SnCl_4(Hg_2Cl_2)$

ANALYSIS

Group II, Tin Division

(40) **Separation of Arsenic.**—Transfer the precipitated sulphides (22), dried by suction or by pressing between filter paper, to a test-tube, and add just 10 cc. of 12N. HCl. (See Discussion 28.) Place the test-tube in a beaker of water and heat until the contents of the tube just begin to boil. Keep the water at this temperature for about ten minutes, occasionally stirring the contents of the tube with a glass rod. When the reaction is complete and no further solution takes place, dilute with 5 cc. of water and filter, allowing the filtrate to run into a 50-cc. graduate. Wash the residue with 5–10 cc. of water, catching the wash water in the graduate with the filtrate. Test the residue for arsenic by (41) and treat the filtrate by (43).

(41) **Detection of Arsenic.**—Punch a hole through the filter and wash the residue of As_2S_5 into a test-tube with 5–10 cc. of 6N. HCl. Warm the mixture gently, adding solid $KClO_3$ or $NaClO_3$, one crystal at a time, until the

arsenic is dissolved. Make the solution just alkaline with NH_4OH, then add about one-third its volume of 15N. NH_4OH and about 0.5 cc. of magnesia mixture ($MgCl_2$–NH_4Cl–NH_4OH). Shake the contents vigorously and if no precipitate forms rub the walls of the tube with a glass rod and allow it to stand for some time. (See note, Preliminary Exp. 14a). The formation of a white crystalline precipitate indicates the presence of arsenic. Filter and confirm the arsenic by (42).

(42) **Confirmatory Test for Arsenic.**—Dissolve the precipitate of $MgNH_4AsO_4$ (41) by pouring 5–10 cc. of 6N. HCl repeatedly through the filter. Heat the solution to boiling and pass H_2S into it for five to ten minutes. The formation of a white precipitate, changing to yellow, shows the presence of arsenic. (See Discussion 17.)

(43) **Detection of Antimony.**—To the filtrate (40) add water just sufficient to make a total volume of 50 cc.; transfer to a small flask and heat to about 90°. Pass H_2S into the hot solution for about five minutes, keeping the temperature at about 90° by placing the flask in a beaker containing boiling water. The formation of an orange-red precipitate shows the presence of antimony. (See Discussion 29.) Filter while hot, add 5 cc. of water, heat to 90° and again saturate with H_2S to remove all antimony. Filter if a precipitate forms, and treat the filtrate by (45).

(44) **Confirmatory Test for Antimony.**—If the precipitate (43) is not orange, and the presence of antimony is doubtful, boil the mixture without filtering until the precipitate has redissolved. Add 5–10 gms. of solid oxalic acid ($H_2C_2O_4$) and pass H_2S into the hot solution. If antimony is present a bright red precipitate will be formed. Filter and test the filtrate for tin by (46).

(45) **Detection of Tin.**—Dilute the filtrate from (43) to 70 cc., cool and pass in H_2S for ten minutes. The formation of a yellow precipitate indicates the presence of tin.

(46) **Confirmatory Test for Tin.**—Boil the mixture (45) or the filtrate from (44) with 1–2 gms. of granulated test lead for two to three minutes. Cool the mixture and filter into a solution of mercuric chloride ($HgCl_2$). The presence of tin is shown by the formation of a white precipitate, which may turn gray if much tin is present. (See Discussion 22.)

Discussion

28. The separation of arsenic, antimony and tin depends on the relative solubility of their sulphides in HCl. It is necessary, therefore, to follow the directions very carefully in order to secure a satisfactory separation. The solubility product of As_2S_5 is considerably smaller than that of Sb_2S_5 or SnS_2; hence it is stable in a much higher concentration of HCl. It is practically insoluble in hot 12N. HCl unless the H_2S formed in the equilibrium

$$As_2S_5 + 10HCl \rightarrow 2(AsCl_5) + 5H_2S$$

is expelled by too vigorous boiling. The hot acid, however, dissolves the tin very readily and the antimony more slowly. In the presence of much antimony some may be left undissolved even in the strong acid, but the amount extracted will never be so small as to escape detection. Also, if the acid becomes much diluted, considerable Sb_2S_5 will be left undissolved. The undissolved portion may be sufficient to give the residue an orange color, but it will not interfere with the test for arsenic.

29. When both antimony and tin are present and the acid concentration is not sufficiently high or the solution has been allowed to cool, some tin may be precipitated with the antimony, in which case the color of the H_2S precipitate will usually be brown.

30. The magnesia mixture used in the detection of arsenic contains a large excess of NH_4^+ for the purpose of reducing the OH^- concentration. This prevents the

precipitation of $Mg(OH)_2$ by the NH_4OH. See Introduction 13, also Appendix I.)

31. Test lead is used for the reduction of tin, rather than zinc or iron, since lead does not reduce tin to the metallic state. If the stronger reducing agent is used the tin will be left in the residue and will have to be dissolved in HCl before being added to the $HgCl_2$ solution.

GROUP III

Preliminary Experiments

Group III, Aluminium Division

$$Al^{+++}, Cr^{+++}, Zn^{++}$$

In connection with the following experiments, study Tables V and VI.

Experiment 17.—Introduce into separate test-tubes 5-cc. portions of the test solutions containing the above ions. Make each distinctly alkaline with NH_4OH, then saturate with H_2S. Heat nearly to boiling to coagulate the precipitates. Write equations.

NOTES.—In the presence of water Al_2S_3 and Cr_2S_3 are completely hydrolized (see Introduction 14); hence the hydroxides formed on the addition of NH_4OH remain unchanged when H_2S is introduced.

Zn^{++} forms with NH_3 the complex ion $Zn(NH_3)_4{}^{++}$. (See Introduction 15.) This removes enough Zn^{++} to prevent the precipitation of $Zn(OH)_2$ but not enough to prevent precipitation of ZnS with H_2S.

Experiment 18.—Decant off the clear liquid from the precipitates of $Al(OH)_3$, $Cr(OH)_3$ and ZnS (Exp. 17) and dissolve in a slight excess of HCl. Add NaOH slowly to alkaline reaction, and then about 1 gram of solid Na_2O_2, a little at a time. (Caution: Do not carry the Na_2O_2 on paper. Use a dry watch glass. Why?) Boil to expel excess Na_2O_2. Write equations.

NOTE.—It should be recalled (see note, Preliminary Exp. 9, also Introduction 15) that a more complete precipitation does not necessarily follow the addition of a reagent in excess of that necessary to reach the solubility product for the compound concerned. The solution of $Al(OH)_3$, as well as that of chromium and zinc, in an excess of NaOH presents another example, but of quite a different type. All three belong to the class known as amphoteric compounds (see Introduction 16). In the presence of excess NaOH, therefore, they form the soluble sodium salts $NaAlO_2$, $NaCrO_2$ and Na_2ZnO_2. Na_2O_2 oxidizes the $NaCrO_2$ to the more readily soluble Na_2CrO_4, but is without effect on $NaAlO_2$ or Na_2ZnO_2. Why?

Experiment 19.—Acidify the solutions of aluminium, chromium and zinc (Exp. 18) with HNO_3 and add NH_4OH to alkaline reaction. Note the precipitation of $Al(OH)_3$. (Difference, separation of Al.) Write equations.

NOTE.—The action of Na_2O_2 in Exp. 18 oxidized the chromium to the more soluble chromate, a compound which does not possess amphoteric properties; hence on the addition of HNO_3 it does not react as a base to form a chromium salt. On the other hand, the aluminium and zinc return to the positive radical as Al^{+++} and Zn^{++} which react with the NH_4OH subsequently added, as outlined in Exp. 17.

Experiment 19a.—Filter off the precipitate of $Al(OH)_3$ (Exp. 19) and wash with water. Dissolve by pouring 5 cc. of 6N. HNO_3 through the filter. Add 4–5 drops of N. 100 $Co(NO_3)_2$ and evaporate nearly to dryness. Soak up the liquid with a small piece of filter paper. Roll it up, wind a platinum wire around it in the form of a spiral and heat in a flame till all the carbon is burnt off. A blue residue is characteristic of aluminium.

NOTE.—The blue substance formed by the interaction of $Co(NO_3)_2$ and $Al(NO_3)_3$ is a compound of CoO and Al_2O_3, probably $Co(AlO_2)_2$, though the exact composition has not been determined. In carrying out the reaction care must be exercised in the addition of $Co(NO_3)_2$. The aluminium must be in excess, otherwise the blue color is hidden by the black cobalt oxide. Furthermore, the presence of sodium or potassium salts causes the mass to fuse and thus interferes with the test. They may be removed by washing the NH_4OH precipitate with water.

Experiment 20.—Acidify the solution of chromium and zinc (Exp. 19) with $HC_2H_3O_2$, and add $BaCl_2$ solution. Note the precipitation of $BaCrO_4$. (Difference, separation of Cr.) Write equations.

Experiment 20a.—Filter off the precipitate of $BaCrO_4$ (Exp. 20) and dissolve it in a very little 6N. HNO_3. Dilute with 9–10 volumes of water and to a portion of it in a test-tube add about 2 cc. of ether and 1 cc. of H_2O_2, and shake.

NOTE.—The blue color in the ether layer is a perchromic acid, probably H_3CrO_7. It is very unstable, decomposing into oxygen and a chromic salt. Excess H_2O_2 or acid accelerates this decomposition.

Experiment 21.—Saturate the zinc solution (Exp. 20) with H_2S. The white flocculent precipitate is ZnS. Filter off the precipitate and dissolve it by pouring 5 cc. of 6N. HNO_3 repeatedly through the filter. Add 4–5 drops of N. 100 $Co(NO_3)_2$ and evaporate in a porcelain dish almost to dryness. Neutralize with Na_2CO_3 solution and add a slight excess. Evaporate to dryness and ignite gently till the purple color of the cobalt disappears. Allow the residue to cool. The green color is due to a compound of the oxides of cobalt and zinc, probably $CoZnO_2$.

NOTE.—ZnS is somewhat more flocculent when precipitated from a warm solution. A white, milky-looking precipitate does not show the presence of zinc. Sulphur often separates out as a white, milky precipitate, especially on standing, or if the current of H_2S is long continued. It is often necessary, therefore, to make the confirmatory test. The addition of too much $Co(NO_3)_2$ must be avoided. (See note, Exp. 19a.)

TABLE V

Outline for the Systematic Analysis of Group III
(Separation into Al and Fe Divisions)

Ions present in acid solution

No.	Reagent	Al^{+++}	Cr^{+++}	Zn^{++}
1	NH_4OH	$(AlOH)_3$	$Cr(OH)_3$	$Zn(NH)_4^{++}$
2	H_2S	$(AlOH)_3$	$Cr(OH)_3$	ZnS
3	HCl	$AlCl_3$	$CrCl_3$	$ZnCl_2$
4	HNO_3	$AlCl_3$	$CrCl_3$	$ZnCl_2$
5	$NaOH$	$NaAlO_2$	$NaCrO_2$	Na_2ZnO_2
6	Na_2O_2	$NaAlO_2$	Na_2CrO_4	Na_2ZnO_2

No.	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}
1	$Mn(OH)_2$	$Fe(OH)_2$	$Co(NH_3)_4^{++}$	$Ni(NH_3)_4^{++}$
2	MnS	FeS	CoS	NiS
3	$MnCl_2$	$FeCl_2$	CoS *	NiS *
4	$MnCl_2$	$FeCl_3$	$CoCl_2$	$NiCl_2$
5	$Mn(OH)_2$	$Fe(OH)_3$	$Co(OH)_2$	$Ni(OH)_2$
6	$MnO(OH)_2$	$Fe(OH)_3$	$Co(OH)_3$	$Ni(OH)_{2-3}$
	↓	↓	↓	↓

* See Note, Exp. 23.

Analysis

Group III

Al^{+++}, Cr^{+++}, Zn^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}

Precipitation and separation of the aluminium and iron divisions.

(50) **Precipitation.**—Boil the filtrate from Group II (20) till the H_2S is expelled. Test the vapor with filter paper wet with lead acetate $[Pb(C_2H_3O_2)_2]$ solution. Add NH_4OH in slight excess, and after shaking note whether a precipitate is formed. (See discussion 32.)

Without filtering add 2–3 cc. more NH_4OH and pass in H_2S until, after shaking, the vapors blacken a piece of filter paper moistened with $Pb(C_2H_3O_2)_2$ solution. Heat the mixture nearly to boiling to coagulate the precipitate. Filter and wash the precipitate with water containing about 1 per cent of $(NH_4)_2S$. If filtration is slow the funnel should be kept covered with a watch glass to prevent oxidation to soluble sulphates. The filtrate should be colorless. (See Discussion 33.) Treat the precipitate by (51) and reserve the filtrate for analysis of Group IV (80).

(51) **Separation of Aluminium and Iron Divisions.**— Transfer the Group III precipitate (50) with the filter if necessary, to a porcelain dish, add 5–20 cc. of 6N. HCl and stir for one to two minutes in the cold. Heat the mixture to boiling and if a black residue still remains add a few drops of HNO_3 and boil again. Dilute with 5–10 cc. of water and filter off the residue of sulphur. Evaporate nearly to dryness to remove excess acid, dilute to 10–20 cc., and add NaOH to alkaline reaction, avoiding a large excess. If a very large precipitate forms add 10–20 cc. more water. Cool the mixture and add 1–3 grams of solid Na_2O_2, a little at a time and with constant stirring. (See Discussion 35.) Add about 5 cc. of 3N. Na_2CO_3 solution unless phosphate or the alkaline earth metals are known to be absent. (See Discussion 37.) Boil to decompose excess Na_2O_2; cool, dilute with an equal volume of water and filter with the aid of suction if possible. (See Discussion 36.) Treat the filtrate by (60) and the residue by (70).

Discussion

32. The H_2S is removed and the effect produced by NH_4OH alone is noted, in order to obtain information regarding the presence of aluminium or other insoluble hydroxides. NaOH and Na_2O_2, used later in the analysis, often contain small quantities of silica and aluminium

which tend to make the detection of aluminium more difficult. Any information gained at this point, therefore, may be of considerable importance.

33. Ammonium monosulphide ($(NH_4)_2S$) is sometimes used instead of H_2S in the precipitation of Group III. When this is done some NiS may be dissolved and pass into the filtrate, giving it a brown or nearly black color. The use of H_2S as directed in (50) almost completely prevents this. If, however, $(NH_4)_2S$ is used and the filtrate is brown or nearly black, indicating that some NiS has been dissolved, it may be precipitated by boiling the solution for a few minutes. It should be filtered off and added to the main precipitate.

34. The presence of a considerable amount of ammonium salts not only lessens the solubility of $Al(OH)_3$, but prevents the precipitation of $Mg(OH)_2$ in this group. A sufficient quantity of ammonium salts is usually formed by the neutralization of the acid already in the solution. The presence of ammonium salts decreases the ionization of NH_4OH, owing to the common ion effect. (See Introduction 12.) The solubility product for the hydroxides of Group III and also for $Mg(OH)_2$ is so small that even a slight excess of NH_4OH causes precipitation. In the presence of much ammonium salts, however, the concentration of OH^- is so reduced that its product with that of certain of the metal ions, e.g., Mn^{++} or Mg^{++}, does not reach the solubility product for those compounds. In the cases of ferric, aluminium and chromium ions the solubility product $(C_{M^{+++}} \cdot C^3_{OH^-})$ is so small that the presence of large amounts of ammonium salts does not appreciably affect their solubility. On the other hand, zinc, nickel and cobalt ions unite with NH_3 to form complex ions similar to those of silver and copper. (See note, Exp. 9 also Introduction 15.)

35. Na_2O_2 is a very unstable substance and decomposes slowly, even in a cold solution, oxygen being given off. In a hot solution the decomposition may become explosive.

The peroxide should therefore be added in very small quantities to a cold solution. This may be easily done by transferring a little of it to a dry watch glass and sprinkling it into the solution, stirring constantly. The reaction is known to be complete when a steady stream of gas is evolved after the mixture has been thoroughly stirred. If much chromium is present the Na_2O_2 should be added until the green chromic salt has been entirely changed to the yellow chromate. The solution should be diluted before filtering in order to prevent disintegration of the filter paper by the strong alkali.

36. The separation of the aluminium and iron divisions by means of NaOH, Na_2O_2 and Na_2CO_3 is very satisfactory except in the case of zinc. When much of the iron division is present 15–20 mgs. of zinc may be carried down in the precipitate, so that provision must be made in the iron division for its detection.

37. It should be remembered that the phosphates of barium, strontium, calcium and magnesium are insoluble in alkaline solution, and hence may have precipitated along with Group III, in case phosphate was present in the original material. Na_2CO_3 is used as a reagent in the separation of the aluminium and iron divisions to insure complete precipitation of these elements since their hydroxides are somewhat soluble even in strong NaOH solution. $ZnCO_3$, though insoluble in dilute solutions of Na_2CO_3 alone, is soluble in the presence of NaOH, owing to the formation of the zincate ion (ZnO_2^{-}). Na_2CO_3 also serves to decompose the chromates of the alkaline earths and so prevent the precipitation of chromium.

TABLE VI

OUTLINE OF THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP III (Al DIVISION)

No.	Reagent	$NaAlO_2$	Na_2CrO_4	Na_2ZnO_2
1	HNO_3	$Al(NO_3)_3$	$Na_2Cr_2O_7$	$Zn(NO_3)_2$
2	NH_4OH	$Al(OH)_3$	Na_2CrO_4	$Zn(NH_3)_4(NO_3)_2$
	HNO_3		↓	↓
	$Co(NO_3)_2$	$Co(AlO_2)_2$(?)		
3	$HC_2H_3O_2$	↓	$Na_2Cr_2O_7$	$Zn(NO_3)_2$
4	$BaCl_2$		$BaCrO_4$	$ZnCl_2$
	HNO_3		H_2CrO_4	↓
	Ether			
	H_2O_2		H_3CrO_7(?)	
5	H_2S		↓	ZnS
	HNO_3			$Zn(NO_3)_2$
	$Co(NO_3)_2$			
	Na_2CO_3			$CoZnO_2$(?)

ANALYSIS

Group III, Aluminium Division

(60) **Separation of Aluminium.**—Acidify the filtrate from (51) with 16N. HNO_3 avoiding a large excess; add NH_4OH just to alkaline reaction and then 2–3 cc. more. (See Discussion 38.) The formation of a white flocculent precipitate shows the presence of aluminium. (See Discussion 39.) Heat the mixture almost to boiling to coagulate the precipitate, filter and wash thoroughly with hot water. Unless the precipitate is white and flocculent the confirmatory test should be made. Treat the filtrate by (62).

(61) **Confirmatory Test for Aluminium.**—Dissolve the precipitate (60) in 5 cc. of 6N. HNO_3; add 4–5 drops of N. 100 $Co(NO_3)_2$ or less if the precipitate was small, evaporate almost to dryness and add 1–2 cc. of water. Absorb the solution in a small piece of filter paper, wind

a platinum wire around it in the form of a spiral and ignite the paper in a flame until the carbon is completely burned. A blue residue shows the presence of aluminium. (See note, Exp. 19a.)

(62) **Detection of Chromium.**—To the filtrate form (60) add $HC_2H_3O_2$ slowly until the solution is just acid. (Test with litmus.) If the solution is colorless, chromium is absent and the solution should be tested for zinc according to (64). If the solution is at all yellow, add about 10 cc. of $BaCl_2$ solution and heat the mixture to boiling. If a yellow precipitate forms, chromium is present. Unless the precipitate is distinctly yellow the confirmatory test should be made. (See Discussion 40.) Treat the filtrate by (64).

(63) **Confirmatory Test for Chromium.**—Dissolve the precipitate (62) by pouring repeatedly through the filter a cold 10-cc. portion of 0.6N. HNO_3. To the solution contained in a test-tube add 1–2 cc. of ether and 1 cc. of 3 per cent H_2O_2 solution. Shake the mixture. A blue color appearing in the ether layer shows the presence of chromium. (See note, Exp. 20a.)

(64) **Detection of Zinc.**—Warm the $HC_2H_3O_2$ solution (62) or the filtrate from (62) to about 50° and saturate in a small flask with H_2S. If a flocculent precipitate does not form at once, cork the flask and allow it to stand five to ten minutes. The formation of a white flocculent precipitate shows the presence of zinc. Unless the precipitate is white and flocculent the confirmatory test should be made.

(65) **Confirmatory Test for Zinc.**—Filter off the precipitate obtained in (64) and dissolve it by pouring repeatedly through the filter a 5-cc. portion of 6N. HNO_3. To the resulting solution add 4–5 drops of N. 100 $Co(NO_3)_2$, or less if the precipitate was small. Evaporate the mixture almost to dryness in a porcelain dish, neutralize with Na_2CO_3 solution and add 0.5 cc. in excess. Evaporate to dryness and ignite gently until the purple color

due to the $Co(NO_3)_2$ disappears. (See Discussion 41.) The appearance of a green color shows the presence of zinc.

Discussion

38. In the separation of aluminium a large excess of NH_4OH must be avoided, since it tends to redissolve the $Al(OH)_3$ by forming NH_4AlO_2. A moderate excess, however, must be present in order to keep the zinc in solution.

39. Since aluminium and silica are often present in the Na_2O_2 and NaOH used as reagents in the separation of the aluminium and iron divisions, a blank test should be made for these impurities by treating 10–15 cc. of water, to which has been added about the same quantities of these two reagents as was used in the regular analysis, by (60) and comparing the precipitate formed with that obtained in the regular analysis. The confirmatory test should always be made in case the NH_4OH precipitate is small, in order to avoid mistaking silicic acid (H_2SiO_3) for $Al(OH)_3$.

40. If, owing to careless manipulation in filtering and washing the second or third group precipitates, and sulphides have been oxidized to sulphates, the addition of $BaCl_2$ for the separation of chromium may give a white or pale yellow precipitate composed largely of $BaSO_4$. This not only makes it necessary to confirm the presence of chromium but renders the confirmatory test less delicate owing to the difficulty of extracting the barium chromate ($BaCrO_4$) from the $BaSO_4$ with acid. The color of the solution after treatment with NaOH and Na_2O_2 for the separation of aluminium and iron divisions should be noted. A yellow color, changing to orange on the addition of acid, indicates chromium.

41. The confirmatory test for zinc is of value only when the H_2S precipitate is small and finely divided or when the presence of foreign materials causes it to be

dark-colored. In the hands of the careful worker the test is quite satisfactory and will detect 0.5 mg. of zinc. If, owing to too much heat, the residue becomes black, it should be dissolved in a few drops of HNO_3 and evaporated almost to dryness, and the test should be repeated with the exception that no more $Co(NO_3)_2$ should be added.

Prelminary Experiments

Group III, Iron Division

Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}

In connection with the following experiments study Tables V and VII.

Experiment 22.—To separate 5-cc. portions of the test solutions containing the above ions, add NH_4OH to alkaline reaction and saturate with H_2S. Note the color of the precipitates formed. Write equations.

Experiment 23.—Decant or filter off the liquid from the precipitates (Exp. 22) and dissolve by the addition of HCl. Add a few drops of HNO_3 if HCl fails to effect a solution. Write equations.

NOTE.—CoS and NiS are dissolved very slowly by HCl but much more rapidly in aqua regia. The oxidizing action of aqua regia removes the $S^{=}$, thus shifting the equilibrium and allowing the cobalt and nickel to pass into solution.

Experiment 24.—To the clear solutions (Exp. 23) add NaOH to alkaline reaction and then about 1 gram of solid Na_2O_2, a little at a time. Note any changes in the precipitates caused by the Na_2O_2. Boil to expel excess Na_2O_2. Write equations.

NOTE.—Na_2O_2 oxidizes $Mn(OH)_2$ to the less soluble $MnO(OH)_2$, $Fe(OH)_2$ to $Fe(OH)_3$ and $Co(OH)_2$ to $Co(OH)_3$. $Ni(OH)_2$ is only partially oxidized to $Ni(OH)_3$. All these compounds are insoluble in an excess of NaOH, differing in this respect from the hydroxides of the aluminium division.

Experiment 25.—Decant or filter off the liquid from the precipitates (Exp. 24) and add 5–10 cc. of HNO_3. Note the fact that iron, cobalt and nickel hydroxides readily dissolve. Heat the mixture containing the manganese nearly to boiling and add H_2O_2, a few drops at a time, until solution is complete. Write equations.

NOTE.—$MnO(OH)_2$ is not affected by HNO_3 alone, but if reduced to a lower oxide it is dissolved as $Mn(NO_3)_2$. The reduction is readily brought about with H_2O_2, oxygen being evolved.

Experiment 26.—Heat the solutions (Exp. 25) to boiling and add gradually 1–2 grams of solid $KClO_3$ or $NaClO_3$. Boil for a minute or two. Note the precipitation of MnO_2. (Difference, separation of Mn.) Write equations.

Experment 26a.—Filter off the liquid from the MnO_2 (Exp. 26), add 5–10 cc. of 16N. HNO_3 and 1–2 grams of PbO_2. Boil for a minute or two and set aside till the PbO_2 settles. The purple color of the solution is due to $HMnO_4$. Write equations.

Experiment 27.—To the solutions of iron cobalt and nickel (Exp. 26) slowly add NH_4OH to distinctly alkaline reaction. Note the precipitation of $Fe(OH)_3$. (Difference, separation of Fe.)

NOTE.—The $Co(OH)_2$ and $Ni(OH)_2$ at first formed dissolve in an excess of NH_4OH with the formation of the complex ions $Co(NH_3)_4^{++}$ and $Ni(NH_3)_4^{++}$. (See Introduction 15.)

Experiment 27a.—Decant or filter the liquid from the $Fe(OH)_3$ precipitate (Exp. 27) and dissolve it in a small quantity of 6N. HCl. Divide the solution into two parts and add $K_4Fe(CN)_6$ to the one and KCNS to the other. Write equations.

NOTE.—It is important to use HCl as the solvent for $Fe(OH)_3 \cdot HNO_3$ must not be used since the subsequent reaction with KCNS is rendered much less delicate in its presence, NO_2, a common impurity in HNO_3, also giving a red color with KCNS. The test is extremely delicate, and

when only a faint red color is produced the acids used should be tested for iron. The red color is due to the formation of non-ionized ferric thiocyanate [$Fe(CNS)_3$] and the test is therefore rendered more delicate when an excess of the reagent is used. $K_4Fe(CN)_6$ gives with Fe^{+++} a deep-blue precipitate of $Fe_4(Fe(CN)_6)_3$ (Prussian blue).

Experiment 28.—Saturate the solutions of cobalt and nickel (Exp. 27) with H_2S. Decant or filter the liquid from the precipitates of CoS and NiS and dissolve by the addition of HCl and a few drops of HNO_3. Evaporate to 1–2 cc. and just neutralize with NaOH. Add $HC_2H_3O_2$ to very faintly acid reaction, and a considerable excess of potassium nitrite (KNO_2). Note the precipitation of potassium cobaltinitrite ($K_3Co(NO_2)_6$). (Difference, detection of Co.)

NOTE.—In very faintly acid reaction, cobalt produces with KNO_2 a yellow crystalline precipitate of $K_3Co(NO_2)_6$; hence the necessity of neutralizing the strong acid with NaOH and subsequently rendering the solution acid with the weak $HC_2H_3O_2$. The precipitate may form rather slowly. The reaction preceeds as follows:

$$Co(NO_3)_2 + 7KNO_2 + 2HC_2H_3O_2 \rightarrow K_3Co(NO_2)_6 + NO + 2KC_2H_3O_2 + 2KNO_3$$

A part of the KNO_2 is used in oxidizing the cobalt to the trivalent condition. This then unites with the excess KNO_2 to form the complex salt $K_3Co(NO_2)_6$. The $K_3Co(NO_2)_6$ is somewhat soluble in water but much less so in KNO_2 solution, owing to the common ion effect of K^+.

Experiment 29.—To the solution containing nickel (Exp. 28) add NH_4OH to faintly alkaline reaction, heat to boiling to drive off excess NH_3 and then add a few drops of dimethyl-glyoxime. Note the precipitation of nickel dimethyl-glyoxime [$Ni\{(CH_3)_2C_2N_2O_2H\}_2$]. (Difference, detection of Ni.)

TABLE VII

Outline for the Systematic Separation and Detection of Group III (Fe Division)

No.	Reagent	$MnO(OH)_2$	$Fe(OH)_3$	$Co(OH)_3$	$Ni(OH)_2$
1	HNO_3	$MnO(OH)_2$	$Fe(NO_3)_3$	$Co(NO_3)_2$	$Ni(NO_3)_2$
2	H_2O_2	$Mn(NO_3)_2$	$Fe(NO_3)_3$	$Co(NO_3)_2$	$Ni(NO_3)_2$
3	$KClO_3$	MnO_2	$Fe(NO_3)_3$	$Co(NO_3)_2$	$Ni(NO_3)_2$
	HNO_3		↓	↓	↓
	PbO_2	$HMnO_4$			
4	*NH_4OH	↓	$Fe(OH)_3$	$Co(NH_3)_4(NO_3)_2$	$Ni(NH_3)_4(NO_3)_2$
	HCl		$FeCl_3$	↓	↓
	(a) $K_4Fe(CN)_6$		$Fe_4(Fe(CN)_6)_3$		
	(b) KCNS		$Fe(CNS)_3$		
5	H_2S			CoS	NiS
6	$HCl—KClO_3$			$CoCl_2$	$NiCl_2$
7	NaOH		↓		
	$HC_2H_3O_2$				
	KNO_2			$K_3Co(NO_2)_6$	$K_4Ni(NO_2)_6$
8	NH_4OH			↓	
	$(CH_3)_2C_2(NOH)_2$				$Ni(CH_3)_2C_2N_2O_2H)_2$

* If phosphates may be present, the procedure should follow Table VIII.

TABLE VIII

Outline for the Systematic Separation and Detection of Fe, Co and Ni When Phosphates may be Present

Ions present in HNO_3 solution

Reagent	PO_4^{---}	Fe^{+++}	Co^{++}	Ni^{++}
1 (a) $(NH_4)_2MoO_4$	$(NH_4)_3PO_4(MoO_3)_{12}$	Fe^{+++}	Co^{++}	Ni^{++}
(b) HCl				
$+K_4Fe(CN)_6$		$Fe_4(Fe(CN)_6)_3$	Co^{++}	Ni^{++}
(c) $(NH_4OH$				
$+HC_2H_3O_2$				
$(NH_4C_2H_3O_2$				
$+FeCl_3$	$FePO_4$	$Fe(C_2H_3O_2)_3$	Co^{++}	Ni^{++}
2 $NH_4C_2H_3O_2$	↓	$Fe(OH)_2C_2H_3O_2$	$Co(C_2H_3O_2)_2$(?)	$Ni(C_2H_3O_2)_2$(?)
3 H_2S		↓	CoS	NiS

Analysis

Group III, Iron Division

(70) **Precipitation of Manganese.**—Transfer the precipitate obtained in (51) to a porcelain dish, together with the filter if necessary; add 5–20 cc. of 6N. HNO_3, heat nearly to boiling and, if any of the precipitate remains undissolved, add slowly and with constant stirring 3 per cent H_2O_2 solution until the precipitate has completely dissolved. Filter to remove the paper and evaporate almost to dryness. Add 10–15 cc. of 16N. HNO_3, heat to boiling, add 0.5–1 gram of powdered $KClO_3$ and boil gently. If a large precipitate forms add 1–2 grams more $KClO_3$, a small portion at a time. A dark brown or black precipitate shows the presence of manganese. Filter through an asbestos filter (see Discussion 42). Heat the filtrate to boiling and add 0.5 gram more of powdered $KClO_3$. Boil gently. If a precipitate forms add 1–2 grams more $KClO_3$, heat to boiling and filter through the same filter. Wash the precipitate with a little 16 N. HNO_3 which has been freed from the oxides of nitrogen by warming with a little $KClO_3$. Treat the precipitate by (71) and the filtrate by (72).

(71) **Confirmatory Test for Manganese.**—Transfer the precipitate (70) to an evaporating dish, add 1–2 grams of lead dioxide (PbO_2) and 10–15 cc. of 6N. HNO_3. Heat the mixture to boiling and boil for one to two minutes. Then pour into a test-tube and allow the PbO_2 to settle. A purple solution shows manganese to be present

(72) **Detection of Phosphate.** — Heat about one-tenth of the filtrate from (70) to boiling and pour it into about three times its volume of ammonium molybdate [$(NH_4)_2MoO_4$] reagent. (See Discussion 43.) The formation of a fine yellow precipitate shows the presence of phosphate.

If phosphate is shown to be present treat a second one-tenth portion of the filtrate by (75).

If phosphate is absent treat the remaining nine-tenths by (73).

(73) **Separation of Iron in the Absence of Phosphate.**—If phosphate was shown to be absent add NH_4OH to the remaining nine-tenths of filtrate (70) until it is distinctly alkaline and then 4–5 cc. in excess. The formation of a reddish-brown precipitate shows the presence of iron. Filter and wash the precipitate. Treat the filtrate by (77) and the precipitate by (74).

(74) **Confirmatory Test for Iron.**—Dissolve the precipitate (73) by pouring a 5–10 cc. portion of 6N. HCl repeatedly through the filter. To the resulting solution add a few drops of potassium ferrocyanide [$K_4Fe(CN)_6$] solution. A deep-blue precipitate (Prussian blue, $Fe_4(Fe(CN)_6)_3$) shows the presence of iron.

(75) **Detection of Iron in the Presence of Phosphate.**—If phosphate was shown to be present evaporate about one-tenth of the filtrate (70) to dryness, add 1–2 cc. of 12N. HCl and evaporate to dryness again. Dissolve the residue in 5–6 cc. of 6N. HCl and add 5 cc. of potassium thiocyanate (KCNS) solution. A red coloration shows the presence of iron. Treat the remainder of filtrate (70) by (76).

(76) **Removal of Phosphate.**—To the remainder of the filtrate from (70) add NH_4OH slowly and with frequent stirring, until the precipitate formed just fails to redissolve. The solution should not be alkaline. If, owing to the addition of too much NH_4OH, it has become alkaline or a large precipitate separates, $HC_2H_3O_2$ should be added to distinct acid reaction. Add 15 cc. of 3N. $NH_4C_2H_3O_2$ solution and unless the mixture has a brownish-red color add ferric chloride ($FeCl_3$) solution drop by drop, until a brownish-red color is produced. (See Discussion 44.) Transfer the mixture to a 250 cc. flask, add water to make a total volume of about 100 cc. and boil for five minutes, adding more water if a large precipitate separates. Allow the mixture to stand one

to two minutes, filter while still hot and wash with hot water. To the filtrate add 10 cc. of 3N. $NH_4C_2H_3O_2$ solution and boil. If a precipitate separates filter it off through a separate filter and reject. Make the filtrate alkaline with NH_4OH and treat it by (77).

(77) **Separation of Zinc, Cobalt and Nickel.**—Pass H_2S into the filtrate (73) or (76) until, after shaking, the vapors blacken filter paper moistened with lead acetate [$Pb(C_2H_3O_2)_2$] solution. The formation of a black precipitate indicates the presence of nickel or cobalt or both; a white flocculent precipitate indicates zinc. Filter, wash the precipitate with water containing a few drops of $(NH_4)_2S$ and treat it by (77a) unless zinc has already been found; otherwise treat it by (78). Treat the filtrate by (80) if phosphate or much chromium has been found. Otherwise reject it. (See Discussion 45.)

(77a) **Separation of Zinc from Cobalt and Nickel.**—If zinc has already been found this procedure may be omitted and the precipitate from (77) treated directly by (78). If zinc has not already been found, transfer the precipitate (77), with the filter if necessary, to an evaporating dish, add 10–30 cc. of 1N. HCl and stir the cold mixture for about five minutes. Filter, wash the residue and treat it by (78). Boil the filtrate until the H_2S is completely expelled. Make the solution alkaline with NaOH. To the cold solution add, with constant stirring, about 1 cc. of powdered Na_2O_2, a little at a time. Boil to decompose excess Na_2O_2, cool and filter. Unite the residue with that undissolved by the 1N. HCl above and treat by (78). Acidify the filtrate with $HC_2H_3O_2$ and test it for zinc according to (64). (See Discussion 46.)

(78) **Detection of Cobalt.**—Transfer the combined residues from (77a) to a porcelain dish and add 5–15 cc. of 6N. HCl. Heat the mixture nearly to boiling, and while hot sprinkle into it a little powdered $KClO_3$. When the reaction is complete and only a residue of sulphur remains, filter and evaporate the filtrate almost to dryness. Take

up the residue with 1–2 cc. of water and make the solution just neutral with NaOH. (Test with litmus.) Add 2–3 cc. of 6N. $HC_2H_3O_2$ and then 3–5 cc. of potassium nitrite (KNO_2) solution and let the mixture stand, with occasional shaking, for fifteen to twenty minutes. (See Discussion 47.) The formation of a yellow crystalline precipitate shows the presence of cobalt. Filter and treat the filtrate by (79).

(79) **Detection of Nickel.**—Dilute the filtrate from (78) to about 25 cc., add NH_4OH until the solution is just alkaline. Heat to boiling to expel excess NH_3 and then add a few drops of dimethyl-glyoxime [$(CH_3CNOH)_2$] solution, and if a red precipitate or coloration does not form at once allow the mixture to stand five to ten minutes. A red precipitate shows the presence of nickel. (See Discussion 48.)

Discussion

42. Owing to the oxidizing action of strong HNO_3, the precipitate of MnO_2 cannot be filtered through an ordinary filter paper. An asbestos filter may be prepared by placing a small pinch of glass wool in the neck of a funnel, tamping it gently with the finger and pouring over it a suspension of fine asbestos fiber in water, enough to make a layer 2–3 mm. thick.

43. If the solution containing the ammonium molybdate is heated much above 60° C., white insoluble molybdic acid (MoO_3) may separate out and render the test for phosphate much less delicate. The yellow precipitate is $(NH_4)_3PO_4 \cdot 12MoO_3$ and is most readily formed at about 60° in the presence of a large excess of $(NH_4)_2MoO_4$ and HNO_3.

44. The separation of ferric iron and phosphate from the bivalent elements is based on the following facts: The solubility product for $FePO_4$ is much smaller than that

for the phosphates of the bivalent elements. In a boiling acetic acid solution containing a large excess of the acetate ion, insoluble basic ferric acetate $[Fe(OH)_2C_2H_3O_2]$ is formed. In order to issure complete removal of the phosphate and prevent its interaction with the bivalent elements excess Fe^{+++} is necessary. This is shown by the brownish-red color of $Fe(C_2H_3O_2)_3$. The separation is satisfactory and complete if accurately carried out. If the solution is allowed to become alkaline much of the iron will precipitate as $Fe(OH)_3$ while the bivalent elements may form insoluble phosphates or hydroxides. On the other hand, if the solution is too acid the $FePO_4$ will not be precipitated owing to the formation of $HPO_4^{=}$ and the consequent reduction of the ion product $C_{Fe^{+++}} \cdot C_{PO_4^{\equiv}}$. If there is a tendency toward the formation of colloidal $FePO_4$ its coagulation may be greatly promoted by boiling.

45. The solution obtained after the removal of zinc, cobalt and nickel may contain some or even all of the alkaline earth metals. In the presence of phosphate, barium, strontium, calcium and magnesium may be precipitated as phosphates along with the metals of Group III. In the presence of much chromium, magnesium may be precipitated completely as $Mg(CrO_2)_2$.

46. Although cobalt and nickel sulphides are soluble in HCl the reaction is comparatively slow even in moderately concentrated solutions. Therefore, when a mixture of the sulphides of zinc, cobalt and nickel is treated with a cold 1N. solution of HCl the greater portion (80–90 per cent) of the cobalt and nickel remains undissolved, while all of the zinc passes into solution. The subsequent treatment of the solution with NaOH and Na_2O_2 gives a very satisfactory separation since the cobalt and nickel are present in such small quantities that only an insignificant amount of zinc is carried down with them.

47. It has been mentioned (see note, Exp. 28) that

when KNO_2 is added to an acid solution containing cobalt and nickel a part of the HNO_2 formed oxidizes the cobalt from the cobaltous (Co^{++}) to the cobaltic (Co^{+++}) state. The cobaltic ion in turn unites with the nitrite ion to form the complex ion $Co(NO_2)_6^{+++}$. In the presence of $HC_2H_3O_2$ the solubility product for $K_3Co(NO_2)_6$ is soon reached, resulting in the precipitation of potassium cobalt-initrite [$K_3Co(NO_2)_6$]. Nickel is not readily oxidized by HNO_2 to the nickelic (Ni^{+++}) state although it does form the complex ion $Ni(NO_2)_6^{++}$. The potassium salt $K_4Ni(NO_2)_6$ is fairly soluble, however, so that little or no nickel is precipitated with the cobalt. Since $K_3Co(NO_2)_6$ is readily soluble in strong acids the necessity of neutralizing the HCl and subsequently acidifying with the weaker $HC_2H_3O_2$ is apparent and since both cobalt and nickel form complex ions with NO_2^- a large excess of KNO_2 must be added.

48. Dimethyl-glyoxime is a weak monobasic organic acid having the formula $(CH_3)_2C_2(NOH)_2$. It reacts with the nickel ion (Ni^{++}) according to the following equation:

$$Ni^{++} + 2 \begin{array}{l} CH_3\text{—}C\text{—}NOH \\ \quad\;\; : \\ CH_3\text{—}C\text{—}NOH \end{array} \rightarrow \begin{array}{l} CH_3\text{—}C\text{—}NOH \quad HON\text{—}C\text{—}CH_3 \\ \quad\;\; : \qquad\qquad\qquad\qquad\;\; : \\ CH_3\text{—}C\text{—}NO\text{—}Ni\text{—}ON\text{—}C\text{—}CH_3 \end{array} + 2H^+$$

Nickel dimethyl-glyoxime is least soluble in a neutral or weakly acid solution, is very voluminous and has an intense red color. It is capable, therefore, of detecting very small quantities (0.1 mg.) of nickel.

In the presence of cobalt, dimethyl-glyoxime produces a brown coloration which deepens as the amount of cobalt is increased. It is advisable, therefore, to remove the cobalt before making the test for nickel.

GROUP IV

Preliminary Experiments

Ba^{++}, Sr^{++}, Ca^{++}

In connection with the following experiments study Table IX.

Experiment 30.—To separate 5-cc. portions of the test solutions containing the above ions add NH_4OH, drop by drop, till its odor persists after shaking. Heat to boiling and then add ammonium carbonate [$(NH_4)_2CO_3$] in slight excess. Allow the precipitates to settle, decant off the liquid and dissolve the precipitates in $HC_2H_3O_2$. Write equations.

Experiment 31.—Divide the solutions (Exp. 30) into two portions each. To one add an equal volume of saturated calcium sulphate ($CaSO_4$) solution. If a precipitate does not form immediately heat to boiling. Note the character of the precipitates and the relative time for precipitation. Write equations.

Experiment 32.—Determine the color of the flame produced by barium, strontium and calcium by introducing a little of each (second portion, Exp. 31) on a clean platinum wire into the colorless flame of the Bunsen burner. (Caution: the platinum wire should be held only in the outer cone of the Bunsen flame.)

Experiment 33.—To the acetic acid solutions of the above metals (second portion, Exp. 31) diluted to about 50 cc. add potassium dichromate ($K_2Cr_2O_7$) solution. Note the precipitation of $BaCrO_4$. (Difference, separation of Ba.) Write equations.

NOTE.—The solubility of the chromates of barium, strontium and calcium in 100 cc. of water at 10° is 0.38, 120 and 400 mgs. respectively From this it is evident that in comparatively dilute solutions practically no strontium or calcium will be precipitated. From more concentrated solutions, however, some strontium may separate out as $SrCrO_4$.

Experiment 34.—To each of the solutions containing strontium and calcium (Exp. 33) add NH_4OH to alkaline reaction, heat to boiling and add $(NH_4)_2CO_3$ in excess. Note the precipitation of $SrCO_3$ and $CaCO_3$. Filter, wash the precipitates and dissolve them by pouring a small quantity of hot $HC_2H_3O_2$ repeatedly through the filter. Write equations.

Experiment 35.—Dilute the solutions (Exp. 34) to 20–25 cc., heat to boiling and add ammonium sulphate [$(NH_4)_2SO_4$] solution. Boil for two to three minutes and filter. To the filtrates add NH_4OH to alkaline reaction and then ammonium oxalate [$(NH_4)_2C_2O_4$] solution. Note the precipitation of CaC_2O_4. (Difference, detection of Ca.) Write equations.

NOTES.—The solubility of the sulphates of strontium and calcium in 100 cc. of water at 18° is 11 and 200 mgs. respectively. The corresponding solubility of their oxalates is 4.6 and 0.56 mgs. From this it will be noted that a complete separation of strontium and calcium cannot be obtained by means of their sulphates, but it is also evident that there will remain in the filtrate enough $CaSO_4$ to be easily detected with $(NH_4)_2C_2O_4$.

The solubility of the salts of barium, strontium and calcium in mgs. per 100 cc. of water at 18° is shown in the following table:

	CO_3	CrO_4	SO_4	C_2O_4
Ba........	2.3	0.38	0.23	8.6
Sr........	1.1	120.	11.	4.6
Ca........	1.3	400.	200.	0.56

TABLE IX

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP IV
Ions present in acid solution

	Reagent	Ba^{++}	Sr^{++}	Ca^{++}
1	$NH_4OH + (NH_4)_2CO_3$	$BaCO_3$	$SrCO_3$	$CaCO_3$
2	$HC_2H_3O_2$	$Ba(C_2H_3O_2)_2$	$Sr(C_2H_3O_2)_2$	$Ca(C_2H_2O_2)_2$
3	(*a*) $CaSO_4$(sat. soln.)	$BaSO_4$	$SrSO_4$	$Ca(C_2H_3O_2)_2$
	(*b*) $K_2Cr_2O_7$	$BaCrO_4$	$SrCrO_4$	$CaCrO_4$
4	$NH_4OH + (NH_4)_2CO_3$	↓	$SrCO_3$	$CaCO_3$
5	$HC_2H_3O_2$		$Sr(C_2H_3O_2)_2$	$Ca(C_2H_3O_2)_2$
6	(*a*) $CaSO_4$(sat. soln.)		$SrSO_4$	$Ca(C_2H_3O_2)_2$
	(*b*) $(NH_4)_2SO_4$		$SrSO_4$	$CaSO_4$
7	$(NH_4)_2C_2O_4$		↓	CaC_2O_4
				↓

ANALYSIS

Group IV

Ba^{++}, Sr^{++}, Ca^{++}

(80) **Precipitation.**—Evaporate the filtrate from Group III (50) to 15–20 cc. Filter off any free sulphur. (See Discussion 49.) Heat to boiling (see Discussion 50), add $(NH_4)_2CO_3$ as long as a precipitate continues to form, and allow the mixture to stand about ten minutes. A white crystalline precipitate indicates the presence of Group IV. Filter, treat the precipitate by (81) and the filtrate by (82). (See Discussion 51.)

(81) **Detection of Barium and Strontium.**—Dissolve the precipitate (80) by pouring a hot 10-cc. portion of 6N. $HC_2H_3O_2$ repeatedly through the filter. To a small portion of the resulting solution add an equal volume of saturated $CaSO_4$ solution. The immediate formation of a white precipitate shows the presence of barium. A white precipitate which forms only slowly or on warming shows the absence of barium and the presence of strontium.

If no precipitate forms, both barium and strontium are absent. (See Discussion 51 and 52.)

If barium is shown to be present, treat the remainder of the solution by (83); if barium is absent and strontium is shown to be present, treat by (85); if both barium and strontium are absent treat by (86).

(82) **Detection of Traces of Barium and Calcium.**—To a portion of the filtrate (80) add 1–2 cc. of $(NH_4)_2SO_4$ and warm. A white precipitate (turbidity) shows the presence of barium. To the remainder of the filtrate (80) add 1–2 cc. of $(NH_4)_2C_2O_4$. A white precipitate (turbidity) shows the presence of calcium. Reunite the two portions, filter off any precipitate and treat the filtrate for Group V by (90). (See Discussion 51.)

(83) **Separation of Barium.**—Dilute the remainder of the solution (81) to about 75 cc. and add 5 cc. of $NH_4C_2H_3O_2$. Heat to boiling, and while hot add $K_2Cr_2O_7$ in slight excess. A large excess should be avoided. (See note, Exp. 33.) Filter while hot and treat the filtrate by (84).

A confirmatory test for barium may be made as follows: Dissolve the precipitate of $BaCrO_4$ in dilute HCl; add about 0.5 cc. of alcohol (C_2H_5OH) and boil until the yellow color entirely disappears and the solution becomes green. Neutralize with NH_4OH and filter off the $Cr(OH)_3$. Acidify the filtrate with HCl and evaporate nearly to dryness. Introduce a little of this solution on a clean platinum wire into the colorless flame of the Bunsen burner. A green color shows the presence of barium.

(84) **Precipitation of Strontium and Calcium.**—To the filtrate (83) add NH_4OH to alkaline reaction; heat to boiling and add $(NH_4)_2CO_3$ solution in excess. Allow the mixture to stand five to ten minutes and filter. Reject the filtrate. Dissolve the precipitate in a few cc. of 6N. $HC_2H_3O_2$ and test for strontium as outlined in (81).

(85) **Separation of Strontium.**—Dilute the solution (84) to about 20 cc.; heat to boiling and add $(NH_4)_2SO_4$

solution, as long as a precipitate continues to form. Filter and treat the filtrate by (86).

A confirmatory test for strontium may be made as follows: Add to the precipitate of $SrSO_4$ about ten times its volume of solid Na_2CO_3 and 10 cc. of water, and boil three to five minutes. Filter, dissolve the residue in 2–3 cc. of HCl and introduce a small portion of the solution on a clean platinum wire into the colorless flame of the Bunsen burner. A deep red color shows the presence of strontium. (Caution: Do not confuse with calcium, yellowish-red color.)

(86) **Detection of Calcium.**—To the filtrate (85) add NH_4OH to alkaline reaction, and then $(NH_4)_2C_2O_4$. A white crystalline precipitate shows the presence of calcium.

A confirmatory test for calcium may be made by moistening the CaC_2O_4 precipitate with a little conc. HCl and introducing a small portion of it on a clean platinum wire into the colorless flame of the Bunsen burner. A yellowish-red color shows the presence of calcium.

Discussion

49. The solution to be tested for Group IV should be clear and colorless and should contain only a moderate excess of NH_4Cl. Any yellow or brown color due to undecomposed $(NH_4)_2S$ or small quantities of nickel or chromium, not precipitated in Group III, will usually be removed by the evaporation as directed in (80). NiS is slightly soluble in excess $(NH_4)_2S$, forming a brown solution. A large excess of NH_4Cl will hold chromium in solution as $CrCl_3 \cdot 4NH_3$, a red solution.

The filtrate from Group III may also contain small quantities of aluminium, owing to its amphoteric (see Introduction 16) nature. Evaporation decomposes $(NH_4)_2S$ and volatilizes excess NH_3 which causes the precipitation

of any NiS and $Al(OH)_3$ that may be present. If the solution is still colored from chromium it should be evaporated to dryness, taken up in 10 cc. of water and filtered to remove excess ammonium salts and $Cr(OH)_3$.

50. Group IV should be precipitated from a hot solution in order to insure complete separation from magnesium, which forms a double salt, $MgCO_3 \cdot (NH_4)_2CO \cdot 4H_2O$, with $(NH_4)_2CO_3$ only moderately soluble in cold water. It is much more soluble in hot water. The solution should not be boiled after the addition of the precipitating agent $(NH_4)_2CO_3$, owing to the fact that it decomposes quite readily when heated. From a cold solution the carbonates are precipitated in a fine state of division. Heat favors the formation of larger particles.

51. Owing to the appreciable solubility of the alkali earth carbonates (see table following note, Exp. 35), traces of these metals may remain in the filtrate after precipitation with $(NH_4)_2CO_3$. The insolubility of their phosphates makes it necessary to remove them before testing for magnesium in Group V.

52. The method of analysis as outlined does not permit a complete separation of barium, strontium and calcium; yet it enables the analyst to determine with a rather high degree of accuracy their presence or absence. The principle involved in the detection of barium and strontium is based on the relative solubility of their sulphates. (See table following notes, Exp. 35.) A saturated solution of $CaSO_4$ produces enough $SO_4^{=}$ to cause an immediate precipitation of $BaSO_4$, but owing to the larger solubility product of $SrSO_4$ the solution is saturated with it only slowly or after heating. The difference in time required for the precipitation of $BaSO_4$ and $SrSO_4$ under the conditions stated is quite marked, so that it is comparatively easy to distinguish between barium and strontium.

53. The test for calcium assumes the absence of strontium and barium and the test for strontium assumes the absence of barium; hence, if barium is shown to be

present it must be removed before making the tests for strontium or calcium. Precipitation as $BaCrO_4$ effectively removes the barium, while little or no $SrCrO_4$ or $CaCrO_4$ are precipitated. (See table following notes, Exp. 35.)

The separation of strontium and calcium with $(NH_4)_2SO_4$ is not complete. Some of the calcium may be precipitated with the strontium and some of the strontium will remain in the solution, though not enough to interfere with the test. Enough calcium will always remain in the filtrate, however, to give a precipitate with $(NH_4)_2C_2O_4$, owing to the very slight solubility of CaC_2O_4.

GROUP V

Preliminary Experiments

Mg^{++}, NH_4^+, K^+, Na^+

In connection with the following experiments study Table X.

Experiment 36.—To 5 cc. of the test solution containing Mg^{++} add an equal volume of NH_4Cl. Make distinctly alkaline with NH_4OH and add sodium phosphate (Na_2HPO_4) solution. The precipitate is $MgNH_4PO_4$. To a second 5-cc. portion of the test solution add NH_4OH to alkaline reaction. Note the precipitation of $Mg(OH)_2$. Now add, without filtering an excess of NH_4Cl. Why does not $Mg(OH)_2$ precipitate in Group III? Explain. Write equations.

Experiment 37.—Evaporate a small quantity of NH_4Cl to dryness in a porcelain dish and heat the residue. To a second portion in a test-tube add NaOH. Note the odor of the gas evolved and its effect upon a piece of moist red litmus paper. What is the gas evolved? Why can this reaction be used as a test for NH_4^+?

Experiment 38.—To separate 1-cc. portions of the test solutions of Mg^{++}, K^{+} and Na^{+} add 10–15 drops of perchloric acid ($HClO_4$). Allow the mixtures to stand for a short time. Note the precipitation of $KClO_4$. (Difference, detection of K.)

Experiment 39.—To separate 1-cc. portions of the test solutions of K^{+} and Na^{+} add an equal volume of alcohol and then about 1 cc. of fluoboric acid (HBF_4). Note the precipitation of KBF_4. (Difference, separation of K.) Write equations.

Experiment 40.—Repeat Exp. 39, substituting fluosilicic acid (H_2SiF_6) for the HBF_4. Note the character of the precipitates formed. Why must potassium be removed before testing for sodium? Write equations.

Experiment 41.—Determine the color of the flame produced by potassium and sodium by introducing a salt of each on a clean platinum wire, into the colorless flame of the Bunsen burner.

TABLE X

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP V

No.	Reagent	Mg^{++}	NH_4^+	K^+	Na^+
1	Na_2HPO_4 NH_4OH	$MgNH_4PO_4$	NH_4^+ *	K^+	Na^+
2	NaOH	↓	NH_3 ↑	K^+	Na^+
3	(a) $HClO_4$			$KClO_4$	$NaClO_4$
	(b) HBF_4			KBF_4	$NaBF_4$
4	H_2SiF_6			↓	Na_2SiF_6

ANALYSIS

Group V

Mg^{++}, NH_4^+, K^+, Na^+

(90) **Detection of Magnesium.**—Evaporate the filtrate from (82) in a porcelain dish until the ammonium salts begin to crystallize out. Filter, and to one-third of the filtrate add 1–2 cc. of Na_2HPO_4 and enough 15N. NH_4OH to make one-third the total volume. Shake the mixture vigorously for two to three minutes, and if a precipitate does not form, rub the walls of the vessel with a glass rod (see note, Exp. 14a) and allow it to stand for some time. A white crystalline precipitate is $MgNH_4PO_4$. (See Discussion 54.) Acidify the remaining two-thirds of the filtrate above with HCl and treat by (91).

If the precipitate of $MgNH_4PO_4$ is of doubtful form it should be filtered, dissolved off the filter with a small quantity of $HC_2H_3O_2$ and reprecipitated by the addition of NH_4OH and a small quantity of $NaHPO_4$.

(91) **Detection of Potassium.**—Transfer the solution (90) to a porcelain dish and evaporate to dryness. Place the dish on a clay triangle and ignite till the ammonium salts are completely expelled. (See Discussion 55.) Dis-

solve the residue in 5–6 cc. of water, transfer about 1 cc. of the resulting solution to a watch glass and add a few drops of perchloric acid ($HClO_4$). The formation of a white crystalline precipitate shows the presence of potassium. Confirm by means of the flame test. (See Preliminary Exp. 41.) Treat the remainder of the solution by (92) if potassium was found, otherwise by (93).

(92) **Removal of Potassium.**—To the remainder of the solution (91) add an equal volume of alcohol and an excess of fluoboric acid (HBF_4). Filter off the precipitate of KBF_4 and treat the filtrate by (93).

(93) **Detection of Sodium.**—To the filtrate (92) add 1–2 cc. of fluosilicic acid (H_2SiF_6) and allow the mixture to stand a few minutes. (See Discussion 58.) A white gelatinous precipitate shows the presence of sodium. Confirm by means of the flame test. (See Preliminary Exp. 41.)

(94) **Detection of Ammonium.**—The test for NH_4^+ must be made on a small portion of the original substance. Introduce 3–4 cc. of the original substance, if it is a liquid, or about 0.1 gm. if it is a solid, into a small beaker, and add NaOH till the mixture is distinctly alkaline. Test the vapors with a piece of red litmus paper placed on the under side of a watch glass covering the beaker. If no change is observed in the litmus, warm the mixture gently, but do not boil. If the red litmus turns blue ammonium salts are present.

Discussion

54. Since there are no characteristic color reactions that can be used for the detection of magnesium it becomes necessary to use considerable care in manipulation in order to secure a precipitate that can be recognized and depended upon. $MgNH_4PO_4$ is a white crystalline substance soluble in $HC_2H_3O_2$, but insoluble in NH_4OH.

Practically all the metals, except alkali metals, form

phosphates insoluble in NH_4OH, hence the necessity of having a clear solution entirely free from metals of the previous groups. The presence of NH_4Cl is necessary to prevent the precipitation of $Mg(OH)_2$, a white flocculent precipitate. (See Discussion 34.)

55. Since the presence of ammonium salts interferes with the subsequent tests for potassium and sodium, it is necessary that their removal be complete. Ammonium compounds react with both $HClO_4$ and H_2SiF_6 to form the corresponding ammonium salts, which are only slightly soluble under the conditions of the experiments. In order to insure the complete volatilization of the ammonium salts all parts of the dish should be well heated, though it must not be heated nearly to redness since both KCl and NaCl are somewhat volatile at that temperature.

56. In testing for potassium and sodium by means of the flame, a faint yellow coloration will almost invariably be obtained, owing to the fact that traces of sodium are nearly always present in the reagents previously used. A fleeting yellow tinge should not be taken as evidence of the presence of sodium, but the yellow color should be distinct and persistent.

57. The color of the flame may be used to detect potassium in the presence of considerable amounts of sodium, if a blue glass is used to cut out the yellow sodium rays. With small amounts of potassium, however, this test is not always satisfactory.

58. Fluosilicic acid (H_2SiF_6) reacts slowly with glass, so that on long standing in a glass vessel it will usually produce a precipitate even in the absence of sodium. Since the Na_2SiF_6 precipitate is semitransparent, the reaction should be carried out in a clear test-tube or on a watch glass.

QUESTIONS FOR REVIEW

1. Name the group reagents and the compounds precipitated by each.

2. Why is a precipitate sometimes obtained on the addition of water before adding the group reagent? Give examples.

3. Why do bismuth and antimony sometimes precipitate in Group I?

4. What is the effect of adding NH_4OH to $AgCl$, Hg_2Cl_2? Write equations.

5. Can HCl be substituted for $NH_4Cl—HNO_3$ in the precipitation of Group I? Explain. Could NaCl be used?

6. Explain what is meant by the following terms: hydrolysis, reagent, precipitate residue, filtrate, colloidal solution.

7. Define ion, acid, base, salt, oxidation, reduction.

8. State the law of mass action.

9. What is meant by common ion, solubility product, ionization constant, complex ion?

10. How may 2N. HCl be made from 6N. HCl?

11. Explain by means of the solubility-product principle why $PbCl_2$ is less soluble in a solution containing NH_4Cl than in pure water.

12. Explain by means of the law of mass action why AgCl is soluble in NH_4OH and is reprecipitated on the addition of an acid.

13. Why is it necessary to have a definite concentration of acid for the precipitation of Group II? What is the effect if the acid concentration is too great, or if it is too small? Explain by means of the solubility-product principle.

14. What precautions must be taken in the treatment of the Group II precipitate with $(NH_4)_2S_x$ reagent! Why?

15. Why is it necessary to test for lead and mercury in both Groups I and II?

16. What are the colors of the following compounds,

precipitated in Group II: HgS, Pbs, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3, SnS, SnS_2?

17. Why is it necessary to evaporate till white fumes appear in the separation of lead in Group II?

18. What is the effect of adding NH_4OH to a solution of $CuSO_4$ and $Bi_2(SO_4)_3$? Write equations. Explain.

19. What is the purpose of KCN in the detection of cadmium? Write equations involved.

20. Explain by means of the solubility-product principle why CuS, which is only slightly soluble in hot 2N. HCl, dissolves readily in hot 2N. HNO_3.

21. What effect does temperature have on the completeness with which Group II sulphides may be precipitated? Explain.

22. What precautions are necessary to insure complete precipitation of arsenic in Group II? Explain.

23. Given a solution which is known to contain no other metals than those given below, outline a method of analysis that will necessitate no unnecessary steps:

(*a*) Lead, mercury, cadmium.

(*b*) Copper, arsenic, cadmium.

(*c*) Bismuth, cadmium, antimony, tin.

24. What is the purpose of $H_2C_2O_4$ in the detection of antimony?

25. Show by a series of equations the changes through which arsenic goes when H_2S is passed through a dilute HCl solution of H_3AsO_4.

26. Explain by means of the solubility-product principle why $PbSO_4$ may be dissolved in $NH_4C_2H_3O_2$ solution.

27. Should $PbCrO_4$ dissolve in $NH_4C_2H_3O_2$ solution? Explain. Why does $PbCrO_4$ precipitate from the same solution that dissolves $PbSO_4$?

28. How is Na_2SnO_2 prepared? Write equations showing all the changes that take place.

29. Explain by means of the law of mass action why the addition of HCl to a solution of $(Na_4)_2SnS_3$ precipitates SnS_2.

30. In the separation of As_2S_5 from Sb_2S_5 and SnS_2 with 12N. HCl why does more As_2S_5 dissolve if the solution is allowed to boil?

31. Why use just 10 cc. of 12N. HCl in the treatment of the sulphides of the tin division?

32. What is the principle on which the separation of antimony and tin, by precipitation with H_2S, is based? Explain by means of the solubility-product principle.

33. What is the confirmatory test for tin? What is the precipitate formed? Write all equations involved.

34. If phosphate is present, what elements may be precipitated on the addition of the third group reagent?

35. Why is it possible to separate the Al division from the Fe division with NaOH and Na_2O_2?

36. What elements are affected by the Na_2O_2? Write equations.

37. Why is Na_2CO_3 added in the separation of the Al and Fe divisions?

38. Why is HNO_3 added before NH_4OH in the separation of aluminium?

39. What is the purpose of H_2O_2 in dissolving the Fe division?

40. If it is necessary to use HNO_3 to dissolve Group III what conclusion can be drawn?

41. Since nickel and cobalt sulphides are not precipitated in acid solution why is it necessary to use aqua regia to dissolve them?

42. Given a solution which is known to contain no other metals than those given below, outline a method of anlysis that will necessitate no unnecessary steps;

(*a*) Aluminium, chromium, iron.

(*b*) Chromium, manganese, cobalt, nickel.

(*c*) Zinc, manganese, iron, nickel.

43. Why is it necessary to test for zinc in the Fe division?

44. If phosphate is present in an unknown, in what

solutions is it necessary to test for the metals of Group IV? Why?

45. What is the purpose of the following reagents in the analysis of Group IV; $CaSO_4$, $K_2Cr_2O_7$, $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$+?

46. Could K_2CrO_4 be used instead of $K_2Cr_2O_7$ in the precipitation of barium and lead? What is the relation between K_2CrO_4 and $K_2Cr_2O_7$?

47. Why is it necessary to add $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to the filtrate from Group IV before testing for Group V?

48. Why does $Mg(OH)_2$ not precipitate in Group III or Group IV? Explain by means of the solubility-product principle.

49. Why not evaporate to dryness and drive off all ammonium salts before testing for magnesium?

50. Why is it necessary to test the original material for NH_4^+?

51. Why remove ammonium salts before testing for potassium and sodium?

52. What is the purpose of HBF_4 in the analysis of Group V?

53. What salts are most suitable for use in flame tests? Why?

54. If an unknown is soluble in water, and phosphate is found, what metals will it be unnecessary to test for?

PART III

ACIDS

In most cases the acid ions (anions) exist in solution as compound radicals composed of two or more elements held together and acting as a single substance. In this respect they differ from the metal ions (cations) which usually exist in solution as simple radicals. The most important anions consisting of a single element are the halides (Cl^-, Br^-, I^-, F^-) and sulphide ($S^=$). Because of this difference, more care must be exercised not only in the preparation of the solution for the detection of acids but also in the treatment during analysis in order to prevent decomposition, oxidation or reduction.

The anions for whose separation and detection provision is made in this scheme of analysis are:

Group I.—Anions whose silver salts are insoluble in cold dilute HNO_3.

Ferrocyanide,	$Fe(CN)_6^{----}$	Sulphide,	S^{--}
Ferricyanide,	$Fe(CN)_6^{---}$	Iodide,	I^-
Thiocyanate,	CNS^-	Bromide,	Br^-
Cyanide,	CN^-	Chloride,	Cl^-

Group II.—Anions whose salts decompose on boiling in acid solution and give characteristic volatile oxides.

Carbonate,	CO_3^{--}	Thiosulphate,	$S_2O_3^{--}$
Sulphite,	SO_3^{--}	Nitrite,	NO_2^-

Group III.—Anions whose silver salts are soluble in acid but insoluble in warm neutral solution.

Arsenite,	AsO_3^{---}	Arsenate,	AsO_4^{---}
Oxalate,	$C_2O_4^{--}$	Phosphate,	PO_4^{---}
Chromate,	CrO_4^{--}	Tartrate,	$C_4H_4O_6^{--}$

Group IV.—Anions whose silver salts are soluble.

Sulphate,	SO_4^{--}	Acetate,	$C_2H_3O_2^-$
Borate,	BO_3^{---}	Nitrate,	NO_3^-
		Fluoride,	F^-

Provision was made for the detection of silicate (SiO_3^{--}) in the course of the analysis for metal ions. (See (5)).

THE SYSTEMATIC ANALYSIS

Anions

Since any interfering cations will be removed during the course of the analysis, the solution as prepared for the metal analysis may be used for the analysis of anions if the substance has been dissolved in water or cold dilute HNO_3. If the substance is a liquid or solution treat directly by (110); if a solid treat by (100).

Preparation of Solution

(100) **Treatment of a Solid.**—To about 0.5 gram of the finely powdered substance add 10 cc. of cold water and mix thoroughly. Filter and wash the residue with 5 cc. of cold water, catching the wash water in the vessel containing the filtrate. Acidify the filtrate with HNO_3, noting if a gas is evolved (see Discussion 60), and treat by (110). Treat the residue by (101).

(101) **Treatment with Dilute HNO_3.**—Pour repeatedly through the filter containing the residue undissolved by cold water, a 5-cc. portion of cold 2N. HNO_3, noting if a gas is evolved. (See Discussion 59.) If a residue remains, punch a hole through the filter and wash it into a test-tube with 5 cc. of 6N. HNO_3. Warm the mixture as long as any of the solid seems to dissolve. Dilute with 5 cc. of water, cool and filter. Treat the combined filtrates by (110). Treat the residue by (102).

(102) **Treatment with Na_2CO_3.**—If there is a residue undissolved by dilute HNO_3, the anion constituents may be dissolved by treatment with Na_2CO_3 solution, as directed in (6) or by fusion with Na_2CO_3 as directed in (7). In either case, however, 6N. HNO_3 should be substituted for HCl, and the solution boiled to drive off the CO_2 before treatment with $AgNO_3$ by (110).

DISCUSSION

59. A careful study of the solubility (see table, Appendix, III) and acidity of the material to be analyzed, in connection with the metal ions found, will often permit the omission of certain steps in the system of analysis for anions. Thus, if the substance contains silver and is soluble in water or dilute acid, it is unnecessary to test for Group I. Barium or lead and sulphate cannot exist together in a neutral water-soluble material. Group II anions will not be present in a strongly acid solution.

A study of the nature and color of the group precipitates may also permit the omission of certain steps; e.g., Ag_2S is black; $Ag_3Fe(CN)_6$, Ag_2CrO_4 and Ag_3AsO_4 are dark red; AgI, Ag_3PO_4 and Ag_3AsO_3 are yellow; AgBr is yellowish-white, while the remaining silver salts of Groups I and III are white.

60. When a strong mineral acid is added to a carbonate, the carbonic acid formed (H_2CO_3) immediately decomposes and, owing to its slight solubility, CO_2, is evolved. Nitrites, sulphites and thiosulphates also tend to decompose in acid solution with the formation of N_2O_3, SO_2, and SO_2+S respectively. The solubility of N_2O_3 and SO_2 is so great, however, that enough will always remain in solution for their detection according to the methods outlined in Group II.

If the evolution of a gas is noted during the treatments as directed in (100) or (101), and carbonate is not found in the solution as prepared, a small portion of the orginal unknown should be tested for carbonate as directed in (130).

TABLE XI

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP I (DIVISION A)

Ions present in dil. HNO_3 solution

No.	Reagent	$Fe(CN)_6^{\equiv}$	$Fe(CN)_6^{=}$	CNS^-	CN^-
1	$AgNO_3$	$Ag_4Fe(CN)_6$	$Ag_3Fe(CN)_6$	AgCNS	AgCN
2	NaCl—HCl	$Na_4Fe(CN)_4$	$Na_3Fe(CN)_6$	NaCNS	NaCN
3	$(NH_4)_2MoO_4$	$Na_2(MoO_2)_3 \cdot (Fe(CN)_6)_3 \cdot 2MoO_3$	$Na_3Fe(CN)_6$	NaCNS	NaCN
4	$Zn(NO_3)_2$ HCl $FeSO_4$	↓	$Zn_3(Fe(CN)_6)_2$ $H_3Fe(CN)_6$ $Fe_3(Fe(CN)_6)_2$	$Zn(CNS)_2$ ↓	$Zn(CN)_2$ ↓
5	$FeCl_3$			$Fe(CNS)_3$	$Fe(CN)_2$
6	NaOH— $FeSO_4$		↓		$Na_4Fe(CN)_6$
7	HCl			↓	$Fe_4(Fe(CN)_6)_3$

ANALYSIS

Group I

$Fe(CN)_6^{\equiv}$, $Fe(CN)_6^{=}$, CNS^-, CN^-, $S^{=}$, I^-, Br^-, Cl^-

(110) **Precipitation.**—To about 25 cc. of the cold solution acidified with HNO_3 (see Discussion 60) add, slowly and with constant stirring, $AgNO_3$ solution in excess. Filter, divide the precipitate into two portions, treat one by (111) and the other by (120). Reserve the filtrate for analysis of Group II (130).

Division A

(111) Solution of the Cyanogen Compounds.—Suspend one portion of the precipitate (110) in 5 cc. of water, add 5 cc. of the NaCl reagent and mix thoroughly. Filter,

reject the residue of silver halides (see Discussion 61) and treat the filtrate by (112). (See Discussion 59.)

(112) **Detection of Ferrocyanide.**—To the filtrate (111) add ammonium molybdate ($(NH_4)_2MoO_4$) reagent in excess. A red flocculent precipitate shows the presence of ferrocyanide. (See Discussion 62.) Filter and treat the filtrate by (113).

(113) **Precipitation of Ferricyanide.**—To the filtrate (112) add a slight excess of $Zn(NO)_3$ solution. Allow the mixture to stand a few minutes. A white precipitate indicates ferricyanide. If the precipitate is colloidal or finely divided shake the mixture with a pinch of asbestos fiber to coagulate the precipitate and filter. Treat the precipitate by (114) and the filtrate by (115).

(114) **Confirmatory Test for Ferricyanide.**—Dissolve the precipitate (113) by pouring a 3-5 cc. portion of 6N. HCl repeatedly through the filter. Dilute the solution with an equal volume of water and add about 1 cc. of $FeSO_4$ solution. A deep blue precipitate shows the presence of ferricyanide.

(115) **Detection of Thiocyanate and Cyanide.**—To the filtrate (113) add about 1 cc. of $FeCl_3$ solution. A red coloration shows the presence of thiocyanate.

Make the solution just alkaline with NaOH and add a few drops of $FeSO_4$ solution. Heat the mixture to boiling and boil gently for one to two minutes. Acidify with HCl to dissolve the hydroxides of iron. A blue residue insoluble in HCl shows the presence of cyanide. (See Discussion 63.)

Discussion

61. The solution of the cyanogen compounds by means of NaCl is based on the relative solubility of their silver salts. The lower solubility product of AgCl causes a displacement of the equilibrium toward the formation of more AgCl and a consequent decrease of Ag^+, with the

result that the ion product of the cyanogen compounds of silver is reduced below their solubility-product value and they pass into solution as sodium salts. In the presence of a small amount of HCl the reaction is rapid and complete. The sulphide and other halides are unaffected, owing to the fact that their solubilities are less than that of AgCl. (See Introduction 12.)

62. The precipitation of ferrocyanide with $(NH_4)_2MoO_4$ reagent is complete only when a considerable excess of $(NH_4)_2MoO_4$ is present. Unless the ferrocyanide is completely removed it will be precipitated with ferricyanide and interfere with the test for that acid. The heavy red precipitate of ferrocyanide is a complex salt of molybdenum with $K_4Fe(CN)_6$, of the probable formula

$$K_2(MoO_2 \cdot Fe(CN)_6)_3 \cdot 2MoO_3 \cdot 20H_2O,$$

and is somewhat soluble in excess of $K_4Fe(CN)_6$. (*Note.*— The student will learn to distinguish between ferrocyanide and ferricyanide by noting that a ferrocyanide contains a complex ion consisting of CN^- and ferrous iron while a ferricyanide contains a complex ion consisting of CN^- and ferric iron.)

63. When a simple cyanide is boiled with NaOH and $FeSO_4$, $Na_4Fe(CN)_6$ is formed. This reacts in acid solution with $FeCl_3$ to form $Fe_4(Fe(CN)_6)_3$ (Prussian blue). Very small quantities of this are not readily detected in the presence of much thiocyanate, but if the solution is filtered a blue precipitate may easily be detected on the filter paper.

TABLE XII

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP I (DIVISION B)

Ions present in dil. HNO_3 solution

No.	Reagent	$S^{=}$	I^-	Br^-	Cl^-
1	$AgNO_3$	Ag_2S	AgI	$AgBr$	$AgCl$
2	HNO_3	Ag_2SO_4	AgI	$AgBr$	$AgCl$
	HCl	H_2SO_4	↓	↓	↓
	$BaCl_2$	$BaSO_4$			
3	$Zn—H_2SO_4$	↓	HI	HBr	HCl
4	$K_2Cr_2O_7$ (cold)		I_2	HBr	HCl
5	$K_2Cr_2O_7$ (hot)		↓	Br_2	HCl
	KI			$KBr(I_2)$	↓
6	$KMnO_4$			↓	Cl_2
	KI				$KCl(I_2)$

ANALYSIS

Division B

(120) **Detection of Sulphide.**—To the second portion (110) add 5 cc. of 6N. HNO_3 and heat to boiling to oxidize the sulphide to sulphate. Cool and filter. Treat the residue by (121). Evaporate the filtrate nearly to dryness, add 1–2 cc. of 6N. HCl, filter and add $BaCl_2$ to the clear filtrate. A white precipitate of $BaSO_4$ shows the presence of sulphide. (See Discussion 64.)

(121) **Solution of the Halides.**—If any of the cyanogen compounds have been found they should be destroyed (see Discussion 65) by placing the residue (120) in a porcelain dish and igniting to dull redness. After the dish and contents have cooled, add a small piece of granulated zinc and 5 cc. of 6N. H_2SO_4. By means of a glass rod loosen any particles adhering to the dish in order to give them free access to the reducing agent. When the reaction is complete and only a black spongy residue

remains, filter, reject the residue of metallic silver and treat the filtrate by (122).

(122) **Detection of Iodide.**—To the cold filtrate (121) add 5 cc. of 6N. H_2SO_4 and 10 cc. of water. Transfer the solution to a test-tube and add about 1 cc. of carbon tetrachloride (CCl_4) and a few drops of $K_2Cr_2O_7$ solution. Shake the mixture thoroughly. The presence of iodide is shown by a violet color in the CCl_4 layer. If iodide is found filter and repeat the treatment with CCl_4 and $K_2Cr_2O_7$ until the CCl_4 layer shows no further coloration. Treat the filtrate by (123).

(123) **Detection of Bromide.**—Transfer the filtrate (122) to a small flask fitted with a delivery tube as shown in Fig. 4. Place 1 cc. of KI solution and about 10 cc. of water in the receiver and connect to the delivery tube as shown. Heat the contents of the reaction flask to boiling and boil for about one minute. Remove the receiver, add 1 cc. of CCl_4 and shake the contents vigorously. A purple coloration in the CCl_4 layer shows the presence of bromide. If bromide is found the boiling should be continued until no further test is obtained with KI solution and CCl_4. Care should be taken to keep the concentration of the acid in the reaction flask near its original value by replacing with water the loss due to evaporation. (See Discussion 66.) If the yellow color should disappear from the solution in the reaction flask a few more drops of $K_2Cr_2O_7$ solution should be added.

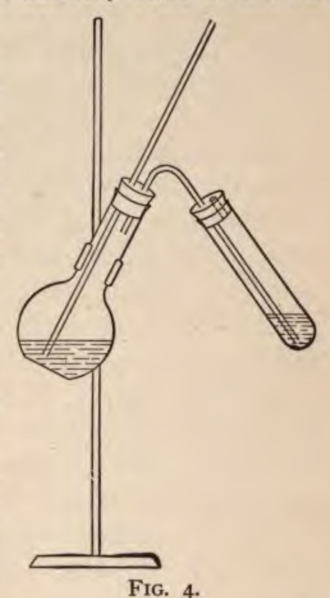


FIG. 4.

(124) **Detection of Chloride.**—To the contents of the reaction flask from which all bromide has been removed

(123), add a few drops of $KMnO_4$ solution and repeat the boiling, at the same time catching the evolved gas in KI solution as outlined in (123) and testing it with CCl_4 as before. A purple color in the CCl_4 layer shows the presence of chloride.

Discussion

64. By the action of boiling HNO_3, according to the equation

$$3H_2S+8HNO_3 \rightarrow 3H_2SO_4+8NO+4H_2O,$$

sulphides are oxidized to sulphates, which may be detected by the white precipitate of $BaSO_4$ produced by $BaCl_2$. Excess HNO_3 should be removed from the solution, however, in order to prevent the possible precipitation of $Ba(NO_3)_2$, a white crystalline precipitate, on the subsequent addition of $BaCl_2$. HCl is added to remove any silver ion that may be in the solution.

The presence of sulphide may be due not only to its presence in the original material but also to the decomposition of thiosulphate. When $AgNO_3$ is added to an acid solution containing a thiosulphate, decomposition of the thiosulphate takes place with the formation of insoluble Ag_2S. When much thiosulphate is present the decomposition is readily detected by more or less rapid change of color in the precipitate from white through varying shades of gray to black.

65. The reduction of the silver halides to metallic silver and the halogen acid by means of zinc and H_2SO_4 is complete only in the absence of the cyanogen compounds. If any of these compounds are found, therefore, they must be removed before the treatment with zinc and H_2SO_4. They are readily destroyed by a dull red heat. A higher temperature might volatilize some silver halide.

66. The separation and detection of the halides is based on their relative resistance to oxidation by $K_2Cr_2O_7$

in acid solution. In a cold 1.5N. H_2SO_4 solution $K_2Cr_2O_7$ readily oxidizes HI. HBr is unattacked by the dichromate in acid concentrations as high as 3N. if the solution is kept cold, but is oxidized when the solution is boiled. Under these conditions HCl remains unchanged but is readily oxidized by the more powerful oxidizing action of $KMnO_4$. It is also slowly oxidized by $K_2Cr_2O_7$ if the acid concentration is allowed to become much greater than 3 N. Hence the necessity of adding water, to keep the solution near its original volume when testing for bromide, is evident.

TABLE XIII

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP II

Ions present in dil. HNO_3 solution

No.	Reagent	$CO_3^{=}$	$SO_3^{=}$	$S_2O_3^{=}$	NO_2^-
1	$Ca(OH)_2$	$CaCO_3$	$CaSO_3$	$CaSO_3$	$Ca(NO_2)_2$
2	HNO_3		H_2SO_3	H_2SO_3	HNO_2
3	$HgNO_3$		$H_2SO_4(Hg)$	$H_2SO_4(Hg)$	HNO_2
4	$FeSO_4$	↓	↓	↓	$FeSO_4 \cdot NO$

ANALYSIS

Group II

$CO_3^{=}$, $SO_3^{=}$, $S_2O_3^{=}$, NO_2^-

(130) **Separation of Group and Detection of Carbonate.**—Transfer the filtrate (110) to a small flask connected with a delivery tube and receiver as shown in Fig. 4. About 10 cc. of lime-water ($Ca(OH)_2$) should be placed in the receiver so that the delivery tube reaches below the surface of the liquid. Heat the solution in the flask to boiling and boil for about one minute. If a milky white precipitate forms in the receiver (see Discussion 67) carbonate is shown to be present. Filter and treat the filtrate by (131). Reserve the solution in the flask for analysis of Group III (140).

(131) **Detection of Sulphite.**—Acidify the filtrate (130) with HNO_3 and add a few drops of mercurous nitrate ($HgNO_3$). A gray precipitate shows the presence of sulphite. (See Discussion 68.) Filter and treat the filtrate by (132).

(132) **Detection of Nitrite**—To the filtrate (131) add about 1 cc. of $FeSO_4$ solution. The appearance of a brown coloration shows the presence of nitrite. (See Discussion 69.)

Discussion

67. When CO_2 is passed through lime-water, insoluble $CaCO_3$ is first formed. Excess of CO_2, however, reacts with the normal carbonate to form soluble $Ca(HCO_3)$. In the detection of carbonate the formation of a white precipitate of $CaCO_3$, which may or may not redissolve, is evidence of the presence of carbonate.

68. Mercurous nitrate ($HgNO_3$) is very readily reduced to Hg by the action of free H_2SO_3, but is unaffected by HNO_2. The reaction proceeds as follows:

$$2HgNO_3 + H_2SO_3 + H_2O \rightarrow 2Hg + H_2SO_4 + 2HNO_3$$

It has been mentioned (see Discussion 64) that $Ag_2S_2O_3$ decomposes even in acid solution with the formation of Ag_2S. The reaction is as follows:

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$$

The decomposition, however, is comparatively slow, and some undecomposed $H_2S_2O_3$ may be left in the filtrate from Group I. Boiling the solution to expel Group II decomposes this with the formation of SO_2 and free sulphur. The detection of both sulphide and sulphite, therefore, may have been due to the presence of thiosulphate in the original material. In this case a portion of the original solution should be tested for sulphide, thiosulphate and sulphite as follows:

To the solution made slightly acid with $HC_2H_3O_2$ add $ZnSO_4$ solution. This will precipitate sulphide as white flocculent ZnS. Filter and treat the filtrate with $Sr(NO_3)_2$ solution and allow the mixture to stand for several hours. The formation of a white precipitate ($SrSO_3$) indicates the presence of sulphite. This may be confirmed by the property of its HCl solution to decolorize iodine solution. The thiosulphate if present, remains in the filtrate from the $SrSO_3$. It can be detected by acidifying with HCl and warming, when sulphur will be deposited.

69. The test for nitrite depends on the formation of brown $FeSO_4 \cdot NO$, according to the following equations:

$$3HNO_3 + 3FeSO_4 + 3HNO_2 \rightarrow Fe_2(SO_4)_3 + Fe(NO_3)_3 + 3NO + 3H_2O$$

$$FeSO_4 + NO \rightarrow FeSO_4 \cdot NO$$

If much $HgNO_3$ was added in testing for sulphite, a white precipitate of Hg_2SO_4 will be formed on the addition of $FeSO_4$.

TABLE XIV

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP III

Ions present in dil. HNO_3 solution

No.	Reagent	$AsO_3^{\equiv}$	$C_2O_4^{=}$	$AsO_4^{\equiv}$	$PO_4^{\equiv}$	$CrO_4^{=}$	$C_4H_4O_6^{=}$
1	$AgNO_3$ $NaOH$	Ag_3AsO_3	$Ag_2C_2O_4$	Ag_3AsO_4	Ag_3PO_4	Ag_2CrO_4	$Ag_2C_4H_4O_6$
2	*$NaOH$ HCl H_2S	Ag_3AsO_3 $AsCl_3$ As_2S_3	$Na_2C_2O_4$	Na_3AsO_4(?)	Na_3PO_4(?)	Na_2CrO_4(?)	$Na_2C_4H_4O_6$
3	$HC_2H_3O_2$ $NaC_2H_3O_2$ $CaCl_2$		CaC_2O_4	Na_3AsO_4	Na_3PO_4	Na_2CrO_4	$Na_2C_4H_4O_6$
4	H_2SO_4 $KMnO_4$ $UO_2(C_2H_3O_2)_2$ HCl H_2S HNO_3 $(NH_4)_2MoO_4$		$H_2C_2O_4$ CO_2	UO_2HAsO_4 H_3AsO_4 As_2S_{3-5}	UO_2HPO_4 H_3PO_4 H_3PO_4 $(NH_4)_3PO_4 \cdot 12MoO_3$	Na_2CrO_4	$Na_2C_4H_4O_6$
5	$NH_4C_2H_3O_2$ $BaCl_2$					$BaCrO_4$	$Na_2C_4H_4O_6$
6	H_2SO_4 $UO_2(C_2H_3O_2)_2$ $KMnO_4$						CO_2

* The compounds marked (?) probably do not exist in the solution as the simple salt, but rather as conplexes with NaOH.

ANALYSIS

Group III

$AsO_3^{\equiv}$, $C_2O_4^{=}$, $AsO_4^{\equiv}$, $PO_4^{\equiv}$, $CrO_4^{=}$, $C_4H_4O_6^{=}$

(140) **Precipitation.**—To the lukewarm solution left in the flask (130) add NaOH drop by drop from a pipette, until, on shaking, the dark Ag_2O precipitate just fails to redissolve. (See Discussion 70.) Filter, treat the precipitate by (141) and reserve the filtrate for analysis of Group IV (150).

(141) **Separation of Arsenite.**—Punch a hole through the filter (140) with a glass rod and wash the precipitate into a graduate cylinder with a small quantity (15–20 cc.) of water. Add 2–3 cc. of NaOH (approximately 6N.) and fill up to the 25 cc. mark with water. (See Discussion 71.) Transfer the contents of the cylinder to a beaker and mix thoroughly. Filter and test the residue for arsenite (142) and treat the filtrate by (143).

(142) **Detection of Arsenite.**—Pour repeatedly through the filter (141) a 5-cc. portion of 6N. HCl to dissolve the arsenite. Saturate the solution with H_2S. A yellow precipitate shows the presence of arsenite. If a dark precipitate is obtained it may be tested for arsenite according to the method outlined for arsenic. (See (21) and following.)

(143) **Separation of Oxalate.**—To the filtrate (141) add a slight excess of $HC_2H_3O_2$ and then about 5 cc. of $NaC_2H_3O_2$ and heat to boiling. To the hot solution add an excess of $CaCl_2$ solution. Mix thoroughly and allow the mixture to stand for two to three minutes. (See Discussion 72.) The formation of a white crystalline precipitate indicates the presence of oxalate. Filter and confirm the oxalate by treating the precipitate (CaC_2O_4) by (144). Treat the filtrate by (145).

(144) **Detection of Oxalate.**—Dissolve the precipitate (143) by pouring 5–6 cc. of 6N. H_2SO_4 repeatedly through the filter. Warm the filtrate and add a drop of $KMnO_4$

solution. If oxalate is present the permanganate will be decolorized.

Optional Method.—Instead of adding $KMnO_4$ transfer the H_2SO_4 solution to a flask (Fig. 4) and boil it, at the same time collecting the evolved gas in lime-water. If oxalate is present it will decompose with the formation of CO_2, which in turn will react with the $Ca(OH)_2$ to form insoluble $CaCO_3$. (See (130)).

(145) **Separation of Arsenate and Phosphate.**—To the filtrate (143) add uranyl acetate $[UO_2(C_2H_3O_2)_2]$ in slight excess. Allow the mixture to stand about five minutes and filter. (See Discussion 73.) Treat the precipitate by (146) and the filtrate by (147).

(146) **Detection of Arsenate.**—Dissolve the precipitate (145) by pouring repeatedly through the filter a 10-cc. portion of 6N. HCl; heat to boiling and saturate with H_2S. The appearance of a white, finely divided precipitate, turning yellow, shows the presence of arsenate. (See Discussion 17.) Filter and treat the filtrate by (147).

(147) **Detection of Phosphate.**—If the presence of phosphate has not already been determined (72), evaporate to dryness the filtrate (146) from which all arsenic has been removed, dissolve the residue in 5 cc. of 16N. HNO_3, and heat to drive off the brown fumes. Pour the resulting solution into about three times its volume of $(NH_4)_2MoO_4$ reagent. The formation of a yellow crystalline precipitate shows the presence of phosphate. (See Discussion 74.)

(148) **Detection of Chromate.**—Heat the filtrate (145) to boiling, and add to the hot solution 5 cc. of $NH_4C_2H_3O_2$ and an excess of $BaCl_2$ solution. The formation of a yellow crystalline precipitate shows the presence of chromate. Unless the precipitate is yellow and crystalline the confirmatory test should be made. (See (63).)

(149) **Detection of Tartrate.**—To the filtrate (148) add about 10 cc. of 6N. H_2SO_4 and filter off the precipitated $BaSO_4$. Transfer the filtrate to a porcelain dish and evaporate to 5–10 cc. The presence of tartrate is indicated

by the ability of the resulting solution to decolorize a drop of $KMnO_4$ solution. (See Discussion 75.)

Discussion

70. The presence of enough silver ions to precipitate all the acids of Group III is shown by the momentary formation of the dark Ag_2O precipitate during the addition of NaOH. The Ag_2O dissolves on shaking, as long as excess acid is present and becomes permanent only when all acid has been neutralized. Its failure to redissolve, therefore, indicates that the neutral point has been reached. If, owing to the precipitation of dark-colored compounds of metals other than silver, the end-point is difficult to detect, it may be ascertained by filtering a small portion and adding a drop of phenolphthalein and then a drop of methyl orange. The solution should remain colorless on the addition of phenolphthalein and change to yellow when methyl orange is added. If the solution should change to red on the addition of phenolphthalein too much NaOH has been added. If this has been done the solution should be acidified with HNO_3 and NaOH again added.

The precipitation should be made in lukewarm solution, since $AgBO_2$ is somewhat insoluble in cold neutral solution.

71. Owing to the formation of complex ions with NaOH. and the slightly soluble Ag_2O, all the silver salts except arsenite are dissolved in an excess of NaOH. Ag_3AsO_3 remains undissolved, even in concentrations as high as 1.5N. NaOH solution, while as much as 250 mgs. of the silver salts of the other acids readily dissolve in 0.5N. NaOH solution.

72. Complete removal of the oxalate is essential, since its presence would later interfere with the detection of tartrate by its reducing action on uranium. Its complete removal is assured only by precipitation from hot solution and subsequent digestion.

73. Arsenate and phosphate form insoluble UO_2HAsO_4 and UO_2HPO_4 respectively, in $HC_2H_3O_2$ solution. Both compounds when present in small amounts tend to pre-

cipitate in colloidal or finely divided form. This is prevented somewhat by precipitation from hot solution or allowing the precipitate to stand. Should the precipitate tend to run through the filter it may be collected and filtered by mixing with a small quantity of asbestos fiber.

74. Both phosphate and arsenate react with $(NH_4)_2MoO_4$ reagent to form insoluble compounds which are very similar in character and color. The complete removal of arsenate is therefore necessary before testing for phosphate. Phosphate is most easily precipitated with $(NH_4)_2MoO_4$ reagent in a strong HNO_3 solution and at a temperature of about 60° C.

75. Uranyl salts are reduced to the green uranous state on boiling a strongly acid solution with tartrate or other reducing agents. On the other hand, in the absence of reducing agents uranyl salts remain unchanged in boiling conc. H_2SO_4. Since oxalate and tartrate are by far the most commonly met of all organic acids capable of reducing the uranyl compounds, the appearance of the green uranous salt on boiling the H_2SO_4 solution is indicative of the presence of tartrate, oxalate having been previously removed. The absence of the green uranous salt, as shown by failure to reduce $KMnO_4$ solution, may be taken as conclusive evidence of the absence of tartrate.

If other organic matter may be present and the uranous salt is obtained in (149), a portion of the original material may be tested for tartrate as follows: Make the somewhat concentrated solution slightly alkaline with NH_4OH, add $CaCl_2$ solution in excess, and allow the mixture to stand a short time. If a precipitate forms filter and digest the precipitate with cold NaOH solution. Dilute slightly, filter, and boil the filtrate. If a precipitate forms, filter while hot, wash the precipitate and transfer it to a test-tube. Add a drop of NH_4OH and a little $AgNO_3$ solution, and warm. The presence of tartrate is shown by the formation of a black precipitate or silver mirror on the walls of the tube.

TABLE XV

OUTLINE FOR THE SYSTEMATIC SEPARATION AND DETECTION OF GROUP IV

Ions present in neutral solution

No.	Reagent	$SO_4^{=}$	$BO_3^{\equiv}$	$C_2H_3O_2^-$	NO_3^-
1	HCl	H_2SO_4	H_3BO_3	$HC_2H_3O_2$	HNO_3
2	$BaCl_2$	$BaSO_4$	$Ba_3(BO_3)_2$	$Ba(C_2H_3O_2)_2$	....
3	HCl turmeric	↓	(?) Brownish-red color	$Ba(C_2H_3O_2)_2$	....
4	H_2SO_4 C_2H_5OH		↓	$C_2H_5C_2H_3O_2$	....
5	$FeSO_4$ H_2SO_4			↓	$FeSO_4 \cdot NO$

ANALYSIS

Group IV

$SO_4^{=}$, $BO_3^{\equiv}$, $C_2H_3O_2^-$, NO_3^-, F^-

(150) **Detection of Sulphate.**—Evaporate the filtrate (140) to 15–20 cc. Add slowly, and with frequent stirring just enough 6N. HCl to precipitate all the silver; filter and reject the precipitate. To the clear filtrate add $BaCl_2$ solution in excess. The formation of a white crystalline precipitate shows the presence of sulphate. (See Discussion 76.) Treat the filtrate by (151).

(151) **Detection of Borate.**—To just 5 cc. of the filtrate (150) add 5 cc. of 12N. HCl and 2 drops of turmeric solution. Allow the mixture to stand ten minutes. If borate is present the solution will assume a brownish-red color. (See Discussion 77.)

(152) **Detection of Acetate.**—Test a portion of the original substance for acetate as follows: If the substance is a solid add to a small quantity on a watch glass a few drops of conc. H_2SO_4. Mix with a glass rod and note

the odor. If acetate is present in considerable quantity the odor of acetic acid will be apparent. If the substance is a liquid a portion of the slightly alkaline solution should be evaporated to dryness and tested with conc. H_2SO_4 as directed above. (See Discussion 78.)

If small quantities are suspected the following test should be made: To a small portion of the solid, obtained by evaporation if necessary, add about 0.5 cc. of alcohol and 1 cc of conc. H_2SO_4. Heat gently and note the odor. The ethylacetate ($C_2H_5C_2H_3O_2$) formed gives a characteristic pleasant odor.

(153) **Detection of Nitrate.**—Test a portion of the original substance for nitrate as follows: Acidify the solution contained in a test-tube with 6N. H_2SO_4, and add an equal volume of $FeSO_4$ solution. Pour about 2 cc. of conc. H_2SO_4 slowly down the sides of the tube so that it forms a layer at the bottom of the solution. If nitrate is present a brown ring will form in a short time at the juncture of the two liquids. (See Discussion 79.)

(154) **Detection of Fluoride.**—In the absence of silica or silicates the etching test may be made as follows: Mix, with the aid of a piece of wood, about 1 gram of the powdered material in a lead dish or platinum crucible with enough conc. H_2SO_4 to form a thick paste. Cover the dish or crucible with a watch glass that has been coated on the convex side with a thin layer of paraffin through which characters have been scratched. Put a little water in the watch glass to prevent melting the paraffin, and warm the dish or crucible gently, preferably over a water bath, for some time. Remove the watch glass, melt off the paraffin and note whether the parts exposed to the action of the fumes have been attacked. If fluoride is present the glass will be dissolved off or etched in the places that were exposed to the fumes. (See Discussion 80.)

In the presence of silica or silicates it is evident that the etching test cannot be used. If the material can be decom-

posed by conc. H_2SO_4 a portion of the powdered material may be mixed with conc. H_2SO_4 in a test-tube and warmed gently while a drop of water is held on the end of a glass rod in the vapors. If fluoride is present the drop of water will become turbid. (See Discussion 80.)

If the material cannot be decomposed with conc. H_2SO_4 it may be fused with 7–8 times its weight of a mixture of equal parts of sodium and potassium carbonate, the melt extracted with water, filtered, the filtrate acidified with $HC_2H_3O_2$ and the fluoride precipitated by the addition of $CaCl_2$ solution. The above test for fluoride may then be made on the dried precipitate.

Discussion

76. It will be recalled (see Discussion 68) that one of the products obtained by the decomposition of $Ag_2S_2O_3$ is H_2SO_4; hence if thiosulphate has been found, a portion of the original solution made acid with HCl should be used for the sulphate test, instead of solution (150).

77. In order to make sure of the presence of borate when the color is slight, a blank test should be made for comparison. In order to be able to estimate the relative amount present the student should make comparison tests with known amounts of borate. In either case he should take care to make all tests alike, using the same quantities of HCl, alcohol and turmeric, since the shade of color depends to a considerable extent upon the concentrations of these substances.

78. Although acetate, if present in the original solution, would appear in the filtrate from the $BaSO_4$ (150) its detection in that solution would necessitate considerable evaporation which will ordinarily be avoided if the original substance is taken.

79. The test for nitrate is very delicate and accurate except in the presence of certain substances which cover up the ring or form a somewhat similar one. Chromates

are reduced by $FeSO_4$ in acid solution giving a green color while ferro- and ferricyanides give a blue precipitate which makes the detection of the brown ring more difficult. Iodides and bromides are oxidized by the conc. H_2SO_4 and produce a ring somewhat similar to the brown of the nitrate. Chromates may be removed by reduction to chromic salts with SO_2 and precipitation with NH_4OH; the others may be removed by precipitation from slightly acid solution with Ag_2SO_4 solution.

80. Most fluorides are decomposed by conc. H_2SO_4 according to the following equation:

$$CaF_2 + H_2SO_4 \rightarrow \underline{CaSO_4} + H_2F_2$$

The reaction proceeds more rapidly if the mixture is heated, owing to the more rapid removal of the volatile H_2F_2. The H_2F_2 may be recognized by its ability to etch glass or dissolve silica or silicates. In either case volatile silicon tetrafluoride (SiF_4) is formed. When this is brought into contact with water the following reaction takes place:

$$SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + \underline{H_4SiO_4}$$

When silicates undecomposed by conc. H_2SO_4 are fused with a mixture of sodium and potassium carbonates, the silicon reacts to form soluble Na_2SiO_3 and any fluoride present forms soluble Na_2F_2.

QUESTIONS FOR REVIEW

1. What ions are precipitated by $AgNO_3$ in acid solution?

2. Why should the solution be kept cold in precipitating Group I?

3. If a ferricyanide is present what other acids of Group I are not likely to be present? Why?

4. Although it is possible to have all metals in the same solution, this is not possible in the case of acids. Why?

5. Why will NaCl solution dissolve all the cyanogen compounds of silver but have no effect of the corresponding halides?

6. What is the effect of boiling Ag_2S with HNO_3? Write equation.

7. What is the principle on which the detection of chloride, bromide and iodide is based?

8. Why is it necessary to remove all iodide before testing for bromide? Why remove all bromide before testing for chloride?

9. Given a solution which is known to contain no other anions than those given below, outline a method of analysis that will necessitate no unnecessary steps;

(*a*) Ferrocyanide, thiocyanate, cyanide.
(*b*) Sulphide, iodide, chloride.
(*c*) Iodide, bromide, chloride.

10. In driving off the last traces of bromide before testing for chloride, why must the water be replaced as it evaporates?

11. Why is it unlikely that Group II acids will be found in a strongly acid solution?

12. What is the precipitate formed in the test for sulphite? Write equation.

13. Write equations showing the action of HNO_2 on $FeSO_4$.

14. If, while the Group II anions are being distilled off a white precipitate should form in the receiver but should redissolve before the distillation is completed what conclu-

sions could be drawn? Write equations showing the changes.

15. Why should Group III acids be precipitated from a warm solution?

16. What precautions are necessary in the precipitation of Group III?

17. What is the effect of adding an excess of NaOH to the silver salts of Group III?

18. Why should a large excess of NaOH be avoided in the separation of arsenite from the remaining Group III acids?

19. If arsenate is found why must it be completely removed before testing for phosphate?

20. What is the confirmatory test for oxalate? Write equations showing all reactions involved.

21. What is the black precipitate formed on the addition of NaOH during the precipitation of Group III?

22. Why must an excess of $AgNO_3$ be present before precipitating Group III?

23. What method may be used for collecting and filtering a colloidal or finely divided precipitate?

24. Given a solution which is known to contain no other anions than those given below outline a method of analysis that will necessitate no unnecessary steps:

(*a*) Nitrite, arsenite, arsenate.
(*b*) Oxalate, chromate, tartrate.
(*c*) Sulphite, oxalate, chromate.

25. What effect would the presence of shreds of filter paper in the H_2SO_4 solution have on the test for tartrate?

26. Why must all oxalate be removed before testing for tartrate?

27. Could $Ba(NO_3)_2$ be used in the place of HCl and $BaCl_2$ in the test for sulphate?

28. What acids interfere with the test for nitrate? How may they be removed?

29. Describe the test for fluoride.

30. If zinc and barium were found in an unknown soluble in dilute HNO_3, what acids would it be unnecessary to test for?

APPENDIX

I. Preparation of Reagents

Acids:

Acetic, 6N.; Mix 350 cc. of glacial acid with 650 cc. of water.

Fluoboric; dissolve H_3BO_3 in 48 per cent H_2F_2, using a lead or platinum dish, until a test portion will not give a precipitate with $Pb(NO_3)_2$ solution. After cooling add an equal volume of alcohol and just enough fluosilicic acid to precipitate any sodium which may be present as an impurity.

Fluosilicic; pour 48 per cent H_2F_2 upon sand in a lead dish or wax bottle until the sand is barely covered. Allow the mixture to stand for a few hours or until the free H_2F_2 has entirely disappeared. Pour off the liquid and add an equal volume of alcohol.

Hydrochloric, 12N.; use the C.P. acid of commerce (Sp.gr. 1.19),

Hydrochloric, 6N.; mix equal volumes of 12N. HCl and water.

Hydrofluoric, 48 per cent; use the C.P. acid of commerce.

Nitric, 16N.; use the C.P. acid of commerce (Sp.gr. 1.42).

Nitric, 6N.; mix 380 cc. of 16N. HNO_3 with 620 cc. of water.

Perchloric, 6N.; mix 650 cc. of the 60 per cent C.P. acid with 350 cc. of water.

Sulphuric, 96 per cent; use the C.P. acid of commerce (Sp.gr. 1.84).

Sulphuric, 6N.; mix 1 volume of the 96 per cent H_2SO_4 with 5 volumes of water.

Bases:

Ammonium hydroxide, 15N.; use the C.P. solution of commerce (Sp.gr. 0.90).

Ammonium hydroxide, 6N.; mix 400 cc. of the 15N. NH_4OH with 600 cc. of water.

Calcium hydroxide, saturated solution; shake 5–10 grams of C.P. CaO with 1000 cc. of water until saturated, and filter.

Sodium hydroxide, 6N.; dissolve 250 grams of pure NaOH in enough water to make a total volume of 1000 cc.

Salts:

Ammonium acetate, 3N.; mix equal volumes of 6N. $HC_2H_3O_2$ and 6N.NH_4OH, or dissolve 250 grams of C.P. $NH_4C_2H_3O_2$ in enough water to make a total volume of 1000 cc.

Ammonium carbonate, 9N.; dissolve 250 grams of freshly powdered $(NH_4)_2CO_3$ in enough cold 6N. NH_4OH to make 1000 cc.

Ammonium chloride, 1N.; dissolve 54 grams of NH_4Cl in enough water to make a total volume of 1000 cc.

Ammonium molybdate; dissolve 75 grams of C.P. $(NH_4)_2MoO_4$ in 500 cc. of water and pour the solution slowly into 500 cc. of 6N. HNO_3. If a precipitate should form, shake the mixture occasionally until solution is complete.

Ammonium oxalate, 0.5N.; dissolve 35 grams of $(NH_4)_2C_2O_4 \cdot H_2O$ in enough water to make a total volume of 1000 cc.

Ammonium polysulphide; saturate 500 cc. of 6N. NH_4OH with H_2S gas, and add to this solution 500 cc. more 6N. NH_4OH, 50 cc. of 6N. NaOH and 25 grams of flowers of sulphur. Digest for some hours and filter.

Ammonium sulphate, 1N.; dissolve 66 grams of $(NH_4)_2SO_4$ in 1000 cc. of water.

Ammonium sulphide; saturate 500 cc. of 6N. NH_4OH with H_2S gas and then add 500 cc. more 6N. NH_4OH.

Barium chloride, 1N.; dissolve 120 grams of $BaCl_2 \cdot 2H_2O$ in 1000 cc. of water.

Bromine water; use saturated solution.

Calcium chloride, 1N.; dissolve 150 grams of $CaCl_2 \cdot 6H_2O$ in 1000 cc. of water.

Calcium sulphate; use saturated solution.

Cobalt nitrate, 0.01N.; dissolve 1.5 grams of $Co(NO_3)_2 \cdot 6H_2O$ in 1000 cc. of water.

Dimethylglyoxime, 0.1N.; dissolve 12 grams of the solid in 1000 cc. of 95 per cent alcohol.

Ferric chloride, 1N.; dissolve 90 grams of $FeCl_3 \cdot 6H_2O$ in 1000 cc. of water.

Ferrous sulphate, 1N.; dissolve 140 grams of $FeSO_4 \cdot 7H_2O$ in 1000 cc. of 0.6N. H_2SO_4 and keep in contact with iron nails.

Hydrogen peroxide; 3 per cent solution.

Lead acetate, 0.2N.; dissolve 38 grams of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in 1000 cc. of water.

Mercuric chloride, 0.1N.; dissolve 27 grams of $HgCl_2$ in 1000 cc. of water.

Mercurous nitrate, 0.1N.; dissolve 29 grams of $HgNO_3 \cdot 2H_2O$ in 1000 cc. of water.

Magnesia mixture, 1N.; dissolve 100 grams of $MgCl_2 \cdot 6H_2O$ and 100 grams of NH_4Cl in water, add 50 cc. of 15N. NH_4OH and dilute to 1000 cc.

Potassium cyanide, 1N.; dissolve 65 grams of KCN in 1000 cc. of water.

Potassium dichromate, 1N.; dissolve 147 grams of $K_2Cr_2O_7$ in 1000 cc. of water.

Potassium ferrocyanide, 1N.; dissolve 105 grams of $K_4Fe(CN)_6 \cdot 3H_2O$ in 1000 cc. of water.

Potassium iodide, 0.1N.; dissolve 17 grams of KI in 1000 cc. of water.

Potassium nitrite, 3N.; dissolve 250 grams of KNO_2 in 1000 cc. of water.

Potassium permanganate, 0.1N.; dissolve 16 grams of $KMnO_4$ in 1000 cc. of water.

Potassium thiocyanate, 1N.; dissolve 97 grams of KCNS in 1000 cc. of water.

Silver nitrate, 0.5N.; dissolve 85 grams of $AgNO_3$ in 1000 cc. of water.

Sodium carbonate, 3N.; dissolve 159 grams of Na_2CO_3 in 1000 cc. of water.

Sodium chloride, 1N.; dissolve 58 grams of NaCl in 1000 cc. of water and add 5 cc. of 12N. HCl.

Sodium phosphate, 1N.; dissolve 120 grams of $Na_2HPO_4 \cdot 12H_2O$ in 1000 cc. of water.

Sodium stannite; add NaOH, drop by drop, to a solution of $SnCl_2$ until the precipitate of $Sn(OH)_2$ is just dissolved. The solution must be kept cold to prevent decomposition and oxidation to Na_2SnO_3. Sodium stannite is unstable and must be prepared as needed.

Stannous chloride, 1N.; dissolve 113 grams of $SnCl_2 \cdot 2H_2O$ in 170 cc. of 12N. HCl and dilute to 1000 cc. Keep in bottles containing granulated tin.

Turmeric; shake an excess of turmeric powder with 95 per cent alcohol and filter.

Uranium acetate, 0.1N.; dissolve 20 grams of

$$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$$

in 1000 cc. of water.

Zinc nitrate. 1N.; dissolve 148 grams of $Zn(NO_3)_2 \cdot 6H_2O$ in 1000 cc. of water.

II. Test Solutions

Solutions used in the preliminary experiments should contain equal amounts of the given ions per cc., in order that the student may learn to estimate more accurately

the relative amounts of the constituents in an unknown. The solutions given below when dissolved in the proportions stated will contain 10 mgs, of the ion per cc. of solution.

Ion.	Salt	Grams per liter	Ion.	Salt	Grams per liter
Ag	$AgNO_3$	15.7	Cr	$CrCl_3$	30
Hg	$HgNO_3 \cdot 2H_2O$	15. (*)	Zn	$ZnCl_2$	21
Pb	$Pb(NO_3)_2$	16. (†)	Mn	$Mn(NO_3)_2 \cdot 6H_2O$	52
Hg	$HgCl_2$	13.5	Fe	$FeSO_4 \cdot 7H_2O$	49 (‖)
Bi	$Bi(NO_3)_3 \cdot 5H_2O$	23. (‡)	Co	$CoCl_2 \cdot 6H_2O$	40
Cu	$CuCl_2 \cdot 2H_2O$	21	Ni	$NiCl_2 \cdot 6H_2O$	41
Cd	$CdCl_2 \cdot 2H_2O$	19.5	Ba	$BaCl_2 \cdot 2H_2O$	18
As	$NaAsO_2$	17.3	Sr	$SrCl_2 \cdot 6H_2O$	30
As	$Na_2HAsO_4 \cdot 7H_2O$	41	Ca	$CaCl_2 \cdot 6H_2O$	55
Sb	$SbCl_3$	19. (§)	Mg	$MgCl_2 \cdot 6H_2O$	84
Sn	$SnCl_2 \cdot 2H_2O$	16. (§)	K	KCl	19
Sn	$SnCl_4 \cdot 3H_2O$	22. (§)	Na	NaCl	25
Al	$AlCl_3$	49.			

* Dissolve in 0.6N. HNO_3.
† Double the amount for Group I experiments.
‡ Dissolve in 3N. HNO_3.
§ Dissolve in 350 cc. of 6N. HCl and dilute to 1 liter.
‖ Dissolve in 0.6N. H_2SO_4 and keep in contact with iron nails.

III. TABLE OF SOLUBILITIES

	Oxide	Hydroxide	Ferrocyanide	Ferricyanide	Thiocyanate	Cyanide	Sulphide	Ioidide	Bromide	Chloride	Carbonate	Sulphite	Nitrite	Arsenite	Oxalate	Arsenate	Phosphate	Chromate	Tartrate	Sulphate	Borate	Acetate	Nitrate	Fluoride	Silicate
Silver	a		i	i	i	i	i*	i	i	i	a	a	w	a	a	a	a	a	a	wa	a	w	w	w	
Mercury(ous)	i						i†	a	a	a	a			a	a	a	a	a	wa	wa		wa	w	a	
Mercury(ic)	a						i†	a	w	w	a			a	a	a	a	wa	a	wa	a	w	w	a	
Lead	a	a	a	wa	a	a	a‡	a	wa	wa	a	a	w	a	a	a	a	ai	a	ai	a	w	w	a	a
Bismuth	a	a					a‡	a	wa	wa	a			a	a		a	a	a	wa	a	w	wa	a	
Copper	a	a	i				a‡	w	w	w	a			a	a	a	a	w	w	w	a	w	w	a	a
Cadmium	a	a	i			a	a‡	w	w	w	a			a	a		a	a	wa	w	wa	w	w	wa	a
Antimony	a	a					a	wa	wa	wa				a	a	a	wa	a	wa	a				w	
Tin(ous)	a	a					a	w		w				a	a	a	a	a	a	w	a	w		w	
Tin(ic)	i	a					a	w		w					w	a	a					w		w	
Aluminium	a	a					h	w	w	w					a	a	a		w	w	a	w	w	i	i
Chromium	a	a					h	w	w	w					wa	a	a	a	w	w§	a	w	w	ai	a
Zinc	a	a	ai	a		a	a	w	w	w	a	a			a		a	a	a	w	a	w	w	wa	a
Manganese	a	a	a	i		a	a	w	w	w	a			a	wa	a	a	w	wa	w	a	w	w	wa	a
Iron(ous)	a	a	i	i		ai	a	w	w	w	a			a	a	a	a		wa	w	a	w	w	wa	a
Iron(ic)	a	a	i	w	w			w	w	w	a			a	a	a	a		w	w	a	w	w	a	a
Cobalt	a	a	i	i		ai	a	w	w	w	a			a	a	a	a	a	w	w	a	w	w	wa	a
Nickel	a	a	i	i		ai	a	w	w	w	a		‖	a	a	a	a	a	a	w	a	w	w	wa	a
Barium	w	w	wa		w	wa	w	w	w	w	a	w′		a	a	a	a	a	a	i	a	w	w	ai	a
Strontium	w	w	w		w	w	w	w	w	w	a			a	a	a	a	a	wa	i	a	w	w	a	a
Calcium	w	w	w	w	w	w	w	w	w	w	a			a	a	a	a	wa	a	w	a	w	w	ai	a
Magnesium	a	a	w	w	w	w	w	w	w	w	a			a	a	a	a	a	wa	w	a	w	w	ai	a
Potassium	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w
Sodium	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w
Ammonium	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	w	

w = soluble in water.
a = soluble in acids.
i = insoluble in water and in acids.
h = hydrolizes completely in presence of water.
wa = slightly soluble in water, soluble in acids.
ai = [illegible]

* = oxidized to soluble sulphate by HNO_3.
† = soluble in aqua regia.
‡ = soluble in HNO_3.
§ = soluble in cold water only.
‖ = slightly soluble only.

IV. A List of the More Common Elements with Their Atomic Weights

Name	Symbol	At. Wt.	Name	Symbol	At. Wt.
Aluminium....	Al	27.1	Lithium......	Li	6.9
Antimony.....	Sb	120.2	Magnesium...	Mg	24.3
Arsenic........	As	75	Manganese...	Mn	54.9
Barium.......	Ba	208	Mercury.....	Hg	200.6
Boron.........	B	11	Molybdenum	Mo	96
Bromine.......	Br	79.9	Nickel.......	Ni	58.7
Cadmium.....	Cd	112.4	Nitrogen	N	14
Calcium.......	Ca	40	Oxygen......	O	16
Chlorine.......	Cl	35.5	Phosphorus...	P	31
Chromium.....	Cr	52	Potassium....	K	39.1
Cobalt........	Co	58.9	Silicon.......	Si	28.3
Copper........	Cu	63.5	Silver........	Ag	107.8
Fluorine.......	F	19	Sodium......	Na	23
Gold..........	Au	197.2	Strontium....	Sr	87.6
Hydrogen.....	H	1.008	Sulphur......	S	32
Iodine........	I	126.9	Tin..........	Sn	118.7
Iron..........	Fe	55.8	Uranium.....	U	238.2
Lead	Pb	207.2	Zinc.........	Zn	65.4



